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TRANSACTIONS.

I.—*The Constituents of Rumex Ecklonianus.*

By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

Rumex Ecklonianus, Meisner (*N. O. Polygonaceae*), is an herb indigenous to South Africa, where it is reputed to possess medicinal properties. It is referred to in "A Contribution to South African Materia Medica," by Andrew Smith, 1895, p. 107, and also in the Transactions of the South African Philosophical Society, **18**, part 2, p. 216. A botanical description of the plant will be found in *Linnaea*, 1840, **14**, 493.

The investigation of the above-mentioned plant has resulted in the isolation of a number of crystalline substances, some of which are anthraquinone derivatives, such as have previously been isolated from other members of the *Polygonaceae*. A complete summary of the results obtained will be found at the end of this paper.

EXPERIMENTAL.

The material employed consisted of the entire overground portions of the above-mentioned *Rumex Ecklonianus*, collected at the time of flowering, and was received through the kindness of Mr. G. E. Oliver, of East London, South Africa, who stated that it occurred as a common weed on the banks of rivulets and in

marshy places. It had, however, been incorrectly designated by Mr. Oliver as *Polygonum tomentosum*, var. *glabrum*, but its identity as the first-mentioned plant was ascertained by Mr. E. M. Holmes, F.L.S., who had kindly compared it with specimens in the herbarium at Kew.

A portion (50 grams) of the finely-powdered, dried herb was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 110°, were obtained:

Petroleum (b. p. 35—50°) extracted	0·77 gram	=	1·54 per cent.
Ether	0·51 "	=	1·02 "
Chloroform	0·69 "	=	1·38 "
Ethyl acetate	0·69 "	=	1·38 "
Alcohol	4·07 "	=	8·14 "

Total = 6·73 grams or 13·46 per cent.

After having ascertained by a preliminary experiment that no alkaloid was present, a quantity (11·733 kilograms) of the dried and ground herb was completely extracted by percolation with cold alcohol. The greater part of the alcohol was removed from the resulting extract, when 1·8 kilograms of a thin extract, containing a quantity of black, tarry matter, were obtained.

The entire amount of the above-mentioned extract was mixed with water and distilled with steam until volatile products ceased to be removed. The distillate, which contained a small amount of oil, and also some solid, was extracted with ether, the resulting ethereal liquid being shaken with a solution of sodium carbonate. This treatment removed from the ether a small amount of a substance, which, after being twice crystallised from ethyl acetate, formed yellowish-brown, slender prisms, melting at 159°. This substance dissolved in concentrated sulphuric acid, yielding a golden-yellow liquid, and its alcoholic solution gave with ferric chloride a green colour, which gradually changed to reddish-brown, but the amount obtained was not sufficient for its further examination. The ethereal liquid which had been treated with sodium carbonate yielded, on evaporation, a small amount of an essential oil, which possessed a dark green colour and an odour closely resembling that of the rhubarb of the Pharmacopœias.

The contents of the distillation flask then consisted of a quantity of a dark green resin (A), together with a dark-coloured aqueous liquid. These products were separated while still hot, when, on allowing the liquid to cool, a quantity of a brown resin (B) was deposited. The latter was likewise separated from the aqueous liquid (C).

Examination of the Green Resin (A).

The green resin, which formed a viscid mass, and amounted to 346 grams, was mixed with purified sawdust, and the dried mixture extracted successively in a large Soxhlet apparatus with light petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Green Resin.

This extract, after the complete removal of the solvent, amounted to about 100 grams. It was dissolved in 1.5 litres of ether, and the ethereal liquid shaken with several successive portions of a 5 per cent. solution of ammonium carbonate. During shaking with the first portion of ammonium carbonate solution, a quantity of crystalline substance separated from the ether. This was collected, and its examination will subsequently be described. The further treatment with ammonium carbonate resulted in the formation of inseparable emulsions, owing to the gradual formation of a product in the form of an amorphous, black powder. The deposition of the latter was effected by removing the ether from the emulsion by passing air through the mixture, after which the solid was collected, but no crystalline substance could be obtained from it. The combined alkaline liquids were acidified, when a small amount of a product was precipitated in the form of a yellowish-brown powder. This was crystallised several times from ethyl acetate, and finally from ether, when it was obtained in long, deep golden-coloured needles, melting at 176° , but the amount was too small for analysis.

Isolation of Emodin Monomethyl Ether.

The previously-mentioned crystalline product, which separated from the ether during the first extraction with alkali, was re-crystallised several times from ethyl acetate, with the use of animal charcoal, when it formed handsome, golden-coloured plates, melting at 197° :

0.1257 gave 0.3116 CO_2 and 0.0493 H_2O . $\text{C} = 67.6$; $\text{H} = 4.4$.

$\text{C}_{16}\text{H}_{12}\text{O}_5$ requires $\text{C} = 67.6$; $\text{H} = 4.2$ per cent.

This substance proved to be emodin monomethyl ether, which has previously been obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, 65, 932). Its identity was confirmed by the preparation of its acetyl derivative, which formed long, pale yellow needles, melting at 185 — 186° . Emodin was methylated by Jowett and Potter (Trans., 1903, 77, 1330), who obtained a monomethyl ether, melting at 200° . They con-

sidered, however, that the ether prepared by them differed from the naturally occurring compound, inasmuch as it yielded an acetyl derivative melting at 157° . A specimen of the emodin monomethyl ether prepared by Jowett and Potter being available to us, we compared it directly with the analogous compound obtained from *Rumex Ecklonianus*, when the two substances were found to be identical. A quantity of the synthetical compound was then acetylated, when the above-described acetyl derivative, melting at $185-186^{\circ}$, was obtained. It is evident, therefore, that the natural and synthetical emodin monomethyl ethers are identical, and the low melting point found by Jowett and Potter for the acetyl derivative of the synthetical compound must be attributed to incomplete acetylation. In this connexion it may be noted that the conversion of emodin monomethyl ether into its acetyl derivative takes place only very slowly, unless a powerful condensing agent, such as camphorsulphonic acid, is employed. In order further to confirm the identity of the natural and synthetical compounds, emodin, which was subsequently isolated in the present investigation, was methylated, whereby a monomethyl ether was obtained, which proved to be identical with that occurring in the plant.

The ethereal liquid, which had been extracted with ammonium carbonate, was then shaken with several successive portions of aqueous potassium carbonate. This caused the formation of emulsions, which, after standing for some time, were separated from the ether and repeatedly washed with this solvent. In order to ensure the complete freedom of the potassium carbonate extract from substances insoluble in this alkali, the total quantity of emulsion was acidified and the product extracted with much ether, after which it was again treated with potassium carbonate, the emulsion being separated from the ether and washed as before. This process was twice repeated. The alkaline emulsions were finally acidified, and the product extracted with ether, after which the ethereal liquid was concentrated to a small bulk and treated with light petroleum. This caused the precipitation of a quantity of the previously-mentioned black, amorphous powder, which was removed by filtration. The clear, dark green filtrate was concentrated to a small bulk, when a quantity of a substance separated after some time. This was collected and recrystallised several times from glacial acetic acid, after which it formed colourless leaflets, melting at $56-60^{\circ}$. On analysis it was found to consist essentially of palmitic acid.

The original filtrate from this product evidently contained further

quantities of fatty acids, and in order to separate these from any phenolic substances which might be present, the entire product was esterified by means of alcohol and sulphuric acid. The material was then dissolved in ether and washed with water, after which it was shaken with potassium carbonate solution. The first treatment with this alkali removed only a quantity of tarry product, but the alkaline extracts subsequently obtained were deep red in colour, and, on acidification, yielded some emodin, which was afterwards obtained in larger amount. Extraction of the ethereal solution of the esters with potassium hydroxide removed only a small amount of impure emodin monomethyl ether, but on subsequently washing it with water a large amount of chlorophyll was removed.

Isolation of a Phytosterol, $C_{20}H_{34}O$.

The ethereal solution of the esters which had been freed from substances soluble in alkalis was evaporated, and the residue distilled under diminished pressure. When the greater part of the product had passed over, it was observed that the residue in the distillation flask possessed a very high boiling point, and tended to become solid. The distillation was therefore stopped, and the undistilled material boiled with alcoholic potash. After removing the greater part of the alcohol, water was added, and the mixture extracted with ether. In this way, a substance was obtained which crystallised from a mixture of ethyl acetate and dilute alcohol in colourless plates, melting at 134° :

0.1024, on drying at 110° , lost 0.0048 H_2O . $H_2O = 4.7$.

0.0976 gave 0.2962 CO_2 and 0.1032 H_2O . $C = 82.8$; $H = 11.7$.

$C_{20}H_{34}O, H_2O$ requires $H_2O = 5.8$ per cent.

$C_{20}H_{34}O$ requires $C = 82.8$; $H = 11.7$ per cent.

This phytosterol appeared to be identical with rhamnol, an alcohol which was first isolated by Power and Lees from Kô-sam fruits (*Year Book of Pharmacy*, 1903, 503), and also occurs in the bark of *Rhamnus purshiana* (Jowett, *Proc. Amer. Pharm. Assoc.*, 1904, 299). It is evident, however, that this alcohol must have occurred in the plant in the form of an acid ester, or analogous compound, since the product from which it was obtained was entirely soluble in alkali carbonates.

The esters of the fatty acids, which had been separated from the above-described alcohol by distillation, were examined in connexion with the acids subsequently obtained from the neutral portion of the petroleum extract of the resin.

Isolation of Chrysophanic Acid.

The original ethereal solution of the petroleum extract of the resin, which had been extracted with ammonium and potassium carbonates, was shaken with a solution of potassium hydroxide. This yielded a deep red liquid, which, on acidification, gave a quantity of a yellow powder. The latter was mixed with the material contained in the mother liquors previously obtained during the purification of the emodin monomethyl ether, and the entire product fractionally crystallised many times from a mixture of ethyl acetate and alcohol. A substance was thus obtained which crystallised in deep golden-coloured spangles, melting at 190° :

0.0807 gave 0.2097 CO_2 and 0.0307 H_2O . $\text{C}=70.9$; $\text{H}=4.2$.

$\text{C}_{15}\text{H}_{10}\text{O}_4$ requires $\text{C}=70.9$; $\text{H}=3.9$ per cent.

This substance was thus identified as chrysophanic acid, and its identity was confirmed by the preparation of its acetyl derivative. The latter compound formed bright yellow leaflets, melting at $204-205^{\circ}$.

Dimethyl ether of chrysophanic acid.—It was shown by Jowett and Potter (*loc. cit.*) that chrysophanic acid was not methylated when heated in a sealed tube at 100° with sodium and methyl iodide in the presence of methyl alcohol. It has now been found, however, that methylation does occur if the latter liquid is absent.

Chrysophanic acid (0.2 gram) was dissolved in absolute alcohol, and a solution of 0.04 gram of sodium in the same solvent added. The liquid was then concentrated, when the sodium derivative, which had separated in the form of small, violet-coloured needles, was rapidly collected and dried. This was then heated with dry methyl iodide in a sealed tube at 100° for six hours. After removing the excess of methyl iodide, the residue was acidified with acetic acid and dissolved in chloroform, the solution thus obtained being freed from unchanged chrysophanic acid by means of potassium hydroxide. On removing the solvent, a product was obtained which crystallised from ethyl acetate in yellow prisms, melting at 190° :

0.0956 gave 0.2520 CO_2 and 0.0430 H_2O . $\text{C}=71.9$; $\text{H}=5.0$.

$\text{C}_{17}\text{H}_{14}\text{O}_4$ requires $\text{C}=72.3$; $\text{H}=5.0$ per cent.

Chrysophanic acid dimethyl ether dissolves in cold concentrated sulphuric acid, giving a deep purple solution. It is insoluble in cold aqueous potassium hydroxide, but on boiling with this reagent it slowly dissolves, yielding a red solution, thus indicating that at least one methyl group is gradually removed by the alkali.

The product contained in the mother liquors obtained during

the purification of the chrysophanic acid was found to consist entirely of a mixture of the latter with emodin monomethyl ether, since, after heating at 160° with concentrated sulphuric acid, it was resolved into emodin and chrysophanic acid. The total amount of anthraquinone derivatives present in the petroleum extract of the green resin was 4.5 grams.

Isolation of Ceryl Alcohol.

The ethereal solution of the neutral portion of the petroleum extract of the green resin was evaporated, and the residue boiled with an excess of alcoholic potash. After removing the greater part of the alcohol, water was added, and the unsaponifiable matter extracted with ether. The product so obtained was fractionally distilled under diminished pressure. The portion boiling below $305^{\circ}/20$ mm. was an unsaturated, oily liquid, but the fraction distilling above this temperature gradually solidified. This was crystallised several times from absolute alcohol, when colourless leaflets, melting at 75° , were obtained:

0.0821 gave 0.2466 CO_2 and 0.1031 H_2O . $\text{C}=81.9$; $\text{H}=14.0$.

$\text{C}_{27}\text{H}_{56}\text{O}$ requires $\text{C}=81.8$; $\text{H}=14.1$ per cent.

This substance therefore appeared to be ceryl alcohol.

Some phytosterol was present in the mother liquors from the above-described product, but no pure substance could be isolated from them.

Isolation of Ipuranol, $\text{C}_{23}\text{H}_{38}\text{O}_2(\text{OH})_2$.

The alkaline liquid, from which the unsaponifiable matter had been removed by means of ether, was acidified and distilled with steam, but no volatile acids were obtained. The contents of the distillation flask were then shaken with ether, when a small amount of flocculent matter collected in the lower portion of the ethereal layer. This was separated by filtration, and purified by crystallisation from dilute pyridine with the use of animal charcoal. It was thus obtained as a colourless, minutely crystalline product, which melted at $285\text{--}290^{\circ}$, and yielded an acetyl derivative crystallising in leaflets, which melted at 162° . A comparison of this acetyl derivative with that obtained from ipuranol (Trans., 1908, **93**, 907) rendered it evident that the two substances were identical.

Identification of the Fatty Acids.

The ethereal solution of the fatty acids from which the above-described ipuranol had been separated was evaporated to a small bulk, and treated with a large volume of light petroleum. This

caused the precipitation of a considerable amount of a black, amorphous powder, which was removed by filtration. The fatty acids contained in the filtrate were then distilled under diminished pressure, after which the saturated and unsaturated constituents were separated by means of their lead salts. A quantity (6 grams) of a mixture of palmitic and stearic acids was thus obtained, which melted at 55—56°, together with 18 grams of liquid acids, which had an iodine value of 173·9.

The previously-mentioned ethyl esters of the acids which had occurred in the plant in the free state were then hydrolysed, and the resulting mixture of acids similarly separated into its solid and liquid components, which amounted to 2 grams and 20 grams respectively. The latter product had an iodine value of 169·5. In order to ascertain the constituents of these mixtures of unsaturated acids, 15 grams of both the free and combined liquid acids were together oxidised with potassium permanganate in the manner described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, 1, 360). This resulted in the formation of isolinusic acid and di- and tetra-hydroxystearic acids, the last-mentioned compound predominating. The unsaturated acids therefore consisted of linolic acid, together with smaller amounts of isolinolenic and oleic acids.

Ethereal Extract of the Green Resin.

Isolation of Emodin and Kaempferol.

This extract amounted to 62 grams. A portion of it (about 6 grams) was very sparingly soluble in ether, and formed a nearly black, amorphous powder, from which nothing could be isolated. The ethereal solution of the more readily soluble portion of the extract was first treated with a solution of ammonium carbonate, but this removed only resinous products, from which nothing crystalline could be separated. The ethereal liquid was then shaken with six successive portions of aqueous potassium carbonate. The first of these operations caused the precipitation of a small amount of black tarry matter, which yielded nothing crystalline, but the aqueous, alkaline liquids subsequently obtained possessed a deep red colour, and, on acidification, yielded a brown powder. This was collected and submitted to a number of fractional crystallisations from glacial acetic acid, when it was ultimately resolved into two products. One of these formed pale yellow, acicular crystals, melting at 276°:

0·0688 gave 0·1586 CO_2 and 0·0227 H_2O . $\text{C}=62\cdot9$; $\text{H}=3\cdot7$.

$\text{C}_{15}\text{H}_{10}\text{O}_6$ requires $\text{C}=62\cdot9$; $\text{H}=3\cdot5$ per cent.

Although the total amount of the above-described product did not exceed 0.15 gram, its identity as kaempferol (1:3:4-trihydroxyflavonol) was positively confirmed by the characteristic behaviour of its acetyl derivative. The latter compound, prepared in the usual manner and recrystallised from methyl alcohol, first melted at 121° , then resolidified, and finally fused at 182° (compare Perkin, Trans., 1902, **81**, 587).

The second crystalline compound obtained from the potassium carbonate extract of the portion of the resin soluble in ether formed dark red needles, melting at 255° , and amounted to 1 gram:

0.0803 gave 0.1954 CO_2 and 0.0281 H_2O . $\text{C}=66.4$; $\text{H}=3.9$.

$\text{C}_{15}\text{H}_{10}\text{O}_5$ requires $\text{C}=66.7$; $\text{H}=3.7$ per cent.

The identity of this substance with emodin was confirmed by the preparation of its acetyl derivative, which formed golden-yellow needles, melting at $190\text{--}191^{\circ}$.

Subsequent treatment of the original ethereal liquid with aqueous potassium hydroxide removed about 4 grams of a mixture of chrysophanic acid and emodin monomethyl ether, after which the ethereal liquid contained only small amounts of green resin.

Chloroform, Ethyl Acetate, and Alcoholic Extracts of the Green Resin.

The chloroform, ethyl acetate, and alcoholic extracts of the resin amounted to 60, 50, and 70 grams respectively. They were all examined in an exhaustive manner, but were found to consist entirely of resins.

Examination of the Brown Resin (B).

This resin, which was soluble in hot water, but again separated on allowing its solution to cool, was thoroughly examined, but nothing definite could be isolated from it. In order to ascertain whether it contained a glucoside, a portion of it was submitted to the action of 5 per cent. aqueous sulphuric acid, but no sugar was formed by this treatment.

Examination of the Aqueous Liquid (C).

The original dark-coloured aqueous liquid (C) was evaporated under diminished pressure to about 1.5 litres, and extracted many times with ether. The ethereal liquid thus obtained was treated first with a solution of ammonium carbonate, then with sodium carbonate, and finally with aqueous sodium hydroxide. The first of these reagents removed a small amount of a product in the form of a gum-like mass, but on extracting the latter with suc-

cessive portions of boiling benzene, evidence was obtained of the existence in it of several crystalline substances. The amounts were so small, however, that none of these could be isolated in a state of purity. The sodium carbonate extracts yielded a small amount of emodin, and a little of a compound which formed pale yellow, acicular crystals, melting at 247° . The latter compound appeared to be pure, but the amount was too small for analysis. It dissolved in alkalis, yielding a solution which was at first colourless, but darkened on exposure to the air, whilst its solution in concentrated sulphuric acid exhibited a purple-blue fluorescence. The material removed from the original ethereal liquid by means of alkali hydroxide yielded nothing definite.

In order to search for a glucoside in the aqueous liquid, the latter was further evaporated under diminished pressure, and the resulting syrup submitted to a prolonged process of extraction with absolute alcohol, followed by ethyl acetate, in a manner similar to that successfully employed by Power and Moore for the isolation of *l*-mandelonitrile glucoside from the bark of *Prunus serotina* (Trans., 1909, 95, 257). During this process 80 grams of potassium chloride and a considerable amount of ammonium chloride separated, but no indication could be obtained of the presence of a glucoside. The viscid syrup, representing the organic constituents of the aqueous liquid which were insoluble in ethyl acetate, was then dissolved in water, and treated with an excess of a solution of basic lead acetate. This caused a voluminous precipitate, from which nothing definite could be isolated. The filtrate from the basic lead acetate precipitate was deprived of lead by means of hydrogen sulphide, and concentrated under diminished pressure. The liquid so obtained contained a small amount of a sugar, which yielded *d*-phenylglucosazone (m. p. 214°), and, on keeping for some time, a considerable quantity of ammonium nitrate was deposited, but no other crystalline substance could be obtained from it.

Summary.

The results of the preceding investigation of *Rumex Ecklonianus*, Meisner, may be summarised as follows.

An alcoholic extract of the herb, when distilled with steam, yielded a trace of a substance which formed yellow prisms, melting at 159° , together with a small amount of essential oil. The non-volatile constituents of the extract consisted largely of brown, resinous matter and a product which slowly formed a black, amorphous powder, but the following definite substances were also obtained: Ceryl alcohol; a phytosterol, $C_{20}H_{34}O$, apparently

identical with rhamnol; palmitic, stearic, oleic, linolic, and *iso*-linolenic acids; a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$; kaempferol; chrysophanic acid; emodin; and emodin monomethyl ether; together with traces of other crystalline substances and large amounts of inorganic salts. A sugar which yielded *d*-phenyl-glucosazone was also present in small amount, but no evidence could be obtained of the presence of a glucoside. The emodin monomethyl ether which was isolated was identical with that obtained by Perkin and Hummel from *Ventilago madraspatana* (Trans., 1894, **65**, 932), and with that prepared synthetically by Jowett and Potter (Trans., 1903, **77**, 1330). The *dimethyl ether* of *chrysophanic acid* was prepared, and obtained in yellow prisms, melting at 191° .

The extract from this plant, like many other products containing anthraquinone derivatives, was found to possess a mild purgative action.

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II.—Cyanocarone.

By REGINALD WILLIAM LANE CLARKE and ARTHUR LAPWORTH.

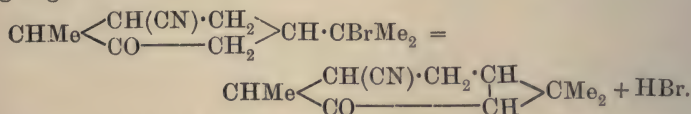
ALTHOUGH carvone and its dihydro-derivative only differ inasmuch as the six-carbon ring in the former contains an ethylenic linking, the products which their hydrobromides yield by loss of hydrogen bromide under the influence of alkalis are quite different in structure, as carone contains a three-carbon and a six-carbon ring, whilst neither nucleus is present in eucarvone, which appears to contain only one seven-membered ring (Wallach, *Annalen*, 1905, **339**, 94, *et seq.*).

The explanation of the formation of eucarvone which most naturally suggests itself is the one indicated by Wallach, namely, that in the first stage of the action of potassium hydroxide on carvone hydrobromide, halogen hydride is removed in the same manner as in the case of dihydrocarvone hydrobromide, but that the molecule of the resulting compound is less stable than that of carone, owing to the additional strain produced by the ethylenic linking, and consequently the *cyclopropane* ring is at once resolved, but between the two carbon atoms which previously formed part of the six-ring of the carvone hydrobromide; hitherto, however, no direct evidence confirming this idea has been forthcoming Had it

been possible to remove two hydrogen atoms from carone, or to separate two groups from adjacent carbon atoms in a substitution product of carone, in such a way as to produce an ethylenic linking at the position where this is found in the hypothetical intermediate compound, it would have been possible to ascertain whether this at once resulted in the formation of eucarvone, and thus to confirm the view referred to, but no substituted derivatives of carone yet appear to have been obtained either by direct substitution or by preparing them from substituted dihydrocarvones.

The investigation of the action of alkalis on cyanodihydrocarvone seemed likely to lead to the formation of such a substituted carvone, and since it has been shown by one of us that β -cyano-derivatives of ketones are frequently convertible into $\alpha\beta$ -unsaturated ketones by the action of alkalis in presence of ferrous hydroxide, a possible mode of attacking this question was promised.

After many unsuccessful attempts, pure cyanocarone was obtained by a method similar to that used in preparing carone from dihydrocarvone, and under certain conditions it was found that cyanodihydrocarvone hydrobromide might be converted nearly quantitatively into the new substance, only traces of cyanodihydrocarvone being regenerated:

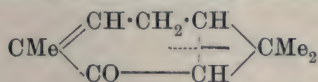


A mixture of isodynamic forms is doubtless produced in the first instance, but in presence of the alkali, which acts as equilibrator, these, during the process of solidification, change with such ease that only one isomeride remains, the equilibrium mixture being saturated with respect to one form.

The product, when nearly pure, crystallises in massive, transparent forms, and has the properties which it might be anticipated a substance having the above constitution would possess. By the action of mineral acids, the *cyclopropane* complex is attacked in all cases before the cyano-group is affected, and with halogen hydrides the first product appears invariably to be the compound of the acid with cyanodihydrocarvone, the reaction above represented taking place in the reverse sense.

The nitrile is saturated in character, and is attacked by cold permanganate solution only with great difficulty, but at the water-bath temperature it is oxidised in alkaline solution, yielding caronic acid, the presence of the dimethyl*cyclopropane* nucleus thus being confirmed. With acid permanganate, another acid, apparently isomeric with caronic acid, but not yet described, is produced.

By the action of alkalis, however, the substance loses the elements of hydrogen cyanide, and if hot dilute aqueous alkali is used in presence of ferrous hydroxide to facilitate this reaction, the volatile product being allowed to pass away at once in the steam, eucarvone is obtained. The product which cyanocarone should normally yield by the action of alkali is the $\alpha\beta$ -unsaturated ketone:

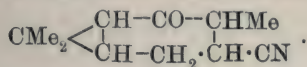


or the hypothetical intermediate product in the preparation of eucarvone from carvone hydrobromide. It follows, therefore, that at 100°, even in presence of quite dilute aqueous alkali, this substance is unstable, and is at once converted into eucarvone. As the cyanocarone certainly contains the *cyclopropane* ring, which is not stable to alkali, it seems certain that the presence of the ethylenic linking in the six-carbon ring to which the *cyclopropane* nucleus is attached does in fact render the molecule unstable, and leads mainly to the opening of the three-carbon ring at the point indicated by the dotted line.

The matter is of further general interest, too, in contrasting the mode in which the *cyclopropane* nucleus breaks down under varying conditions. It would not appear reasonable to suggest that the complex $\cdot\text{CMe}_2\cdot\text{CH}\cdot$ is less stable than $\cdot\text{CH}\cdot\text{CH}\cdot$, as under the influence of halogen hydride it is the former which is resolved. Nor can it be maintained that either is in such a position with reference to the keto- or cyano-group as would render it more liable to attack on this account. It would rather appear that when the carbon ring is saturated there is the less strain when the ring is composed of six atoms, but when there is an ethylenic linking in the nucleus, at least in certain positions, then the reverse obtains, and the smaller ring is the less stable one.

EXPERIMENTAL.

Formation of Cyanocarone,



The hydrobromide of cyanodihydrocarvone, prepared as described by Lapworth (Trans., 1906, 89, 1826), was rapidly crystallised from alcohol, and treated in the following manner. The hydrobromide (160 grams) was suspended in methyl alcohol (300 c.c.), cooled to 0°, and to the pasty mixture an ice-cold solution of potassium hydroxide (36 grams) in methyl alcohol (150 c.c.) was added gradually with frequent agitation. The resulting liquid

was kept for some hours, while it gradually assumed a violet colour, potassium bromide being deposited. The whole was then saturated with carbon dioxide, and the precipitated potassium bromide and bicarbonate separated by filtration; the methyl alcohol was removed by distillation, and the volatile material expelled with the aid of a rapid current of steam. In some experiments the oil remaining in the distillation flask solidified on cooling, but it was found to be advantageous,—as a rule, to shake the semi-solid material for some time with an ice-cold solution of potassium permanganate, added gradually until the colour of the latter was no longer discharged, the excess of permanganate and the precipitated manganese dioxide being subsequently removed by sulphur dioxide. The crude cyanocarone, which solidified on again cooling the liquid, was collected, and crystallised several times from alcohol:

0.2158 gave 0.589 CO_2 and 0.166 H_2O . $\text{C}=74.4$; $\text{H}=8.55$.

0.2206 „ 0.606 CO_2 „ 0.172 H_2O . $\text{C}=74.9$; $\text{H}=8.66$.

0.1264 „ 9.0 c.c. N_2 (moist) at 19° and 757 mm. $\text{N}=8.15$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.6$; $\text{H}=8.47$; $\text{N}=7.92$ per cent.

Cyanocarone is very soluble in ethyl and methyl alcohols, ether, acetone, benzene, or ethyl bromide, fairly so in light petroleum, and almost insoluble in water. It crystallises with great readiness from its alcoholic solution in large, colourless, six-sided, transparent crystals, which melt sharply at $54\text{--}55^\circ$. When strongly heated, cyanocarone boils and distils with some decomposition above 300° .

0.201, made up to 25.05 c.c. with absolute alcohol, at 18° gave, in a 2-dcm. tube, $\alpha_D + 4.79^\circ$, whence $[\alpha]_D + 298^\circ$.

0.2306, made up to 25.1 c.c. with absolute alcohol, at 20° gave, in a 2-dcm. tube, $\alpha_D + 5.45^\circ$, whence $[\alpha]_D + 297^\circ$.

Cyanocarone is only very slowly attacked by a cold aqueous solution of potassium permanganate, or by a solution of the same salt in acetone at the boiling point of the solvent. It does not decolorise a solution of bromine in glacial acetic acid in presence of sodium acetate.

The *semicarbazide*, $\text{C}_{11}\text{H}_{15}\text{N:N}_2\text{H}\cdot\text{CO}\cdot\text{NH}_2$, crystallises from alcohol in thin, flat, rectangular plates, which melt rather indefinitely, and decompose slightly at $218\text{--}221^\circ$:

0.1526 gave 31.6 c.c. N_2 (moist) at 15° and 758 mm. $\text{N}=24.18$.

$\text{C}_{12}\text{H}_{18}\text{ON}_4$ requires $\text{N}=23.93$ per cent.

Cyanocarone also yields an oxime, but this could not be obtained in crystalline form.

Action of Alkali and Ferrous Hydroxide on Cyanocarone.

On boiling cyanocarone with a 10 per cent. sodium hydroxide solution, an oil with a peppermint-like odour is produced, and the aqueous solution gives the reactions of a cyanide. The removal of hydrogen cyanide appears to take place more readily in presence of ferrous hydroxide, and for the investigation of this decomposition the following conditions were employed. Twenty grams of cyanocarone, 12 grams of potassium hydroxide, 4 grams of ferrous chloride, and 150 c.c. of water were gently heated in a flask attached to a condenser, and the water which distilled over, carrying with it the odorous oil, was replaced by gradually adding water to the flask. The process was continued until the aqueous distillate no longer contained an appreciable quantity of oil. The distillate was then saturated with common salt, and the oil extracted with ether. On fractionation, 4.4 grams of liquid boiling between 205° and 208° , and 1.1 grams boiling between 208° and 215° were obtained, a small amount of residue, which underwent decomposition on further heating, remaining in the distilling flask.

The oil thus obtained readily decolorised a solution of bromine, and gave a reddish-violet colour on boiling with methyl-alcoholic potash. It yielded an easily crystallisable semicarbazide, which, on recrystallisation from alcohol, melted at $183\text{--}184^{\circ}$:

0.1978 gave 35.5 c.c. N_2 (moist) at 19° and 751 mm. $\text{N} = 20.38$.

$\text{C}_{11}\text{H}_{17}\text{ON}_3$ requires $\text{N} = 20.29$ per cent.

On mixing this semicarbazide with eucarvone semicarbazide, prepared as described by Wallach and Löhr (*Annalen*, 1899, 305, 237), the mixture melted at $183\text{--}184^{\circ}$; the product, after repeated crystallisation from methyl and ethyl alcohols, was optically inactive. The conversion of cyanocarone into eucarvone by the above process is not quantitative, and a considerable amount of a white substance crystallises out of the aqueous residue. This was isolated by diluting the residual liquid in the flask with water, heating to boiling, and filtering, when, on cooling, the substance separated, and was purified by recrystallisation from water, and finally from alcohol:

0.2278 gave 0.5630 CO_2 and 0.1786 H_2O . $\text{C} = 67.43$; $\text{H} = 8.72$.

0.203 „ 13.3 c.c. N_2 (moist) at 20° and 756 mm. $\text{N} = 7.45$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 67.69$; $\text{H} = 8.72$; $\text{N} = 7.18$ per cent.

The substance has the properties of a saturated lactam or anhydramide, it is unaffected by a cold potassium permanganate solution, or by boiling aqueous or alcoholic potassium hydroxide

solutions, and is only slowly changed by fusion with potassium hydroxide and a few drops of water. It crystallises from water or alcohol in square plates or cubes, melting at 210—212°.

Action of Hydrogen Halides on Cyanocarone.

When heated with concentrated hydrochloric acid on the water-bath, cyanocarone yielded an acidic substance, which appeared to be a mixture of the stereoisomeric dihydrocarvonecarboxylic acids (Trans., 1906, **89**, 1823); from this after repeated crystallisation from carbon tetrachloride and finally ethyl acetate, an unsaturated acid melting at 141—142° was obtained, which was identified by the mixed melting-point method as β -dihydrocarvonecarboxylic acid. With a cold saturated solution of hydrogen chloride, cyanocarone is first converted into a hydrogen chloride additive product identical with that obtained from cyanodihydrocarvone, the cyclopropane ring undergoing fission. This substance on further treatment with hydrochloric acid loses the elements of hydrogen chloride, and the $\cdot\text{CN}$ group is converted into the $\text{CO}\cdot\text{NH}_2$ group, the amide of the unsaturated dihydrocarvonecarboxylic acid being formed. Twenty grams of cyanocarone were suspended in 100 c.c. of concentrated hydrochloric acid, and the mixture was saturated with hydrogen chloride in the cold. The cyanocarone dissolved, and after a short time a white, crystalline substance separated, which was purified by crystallisation from alcohol:

0.3035, after being heated with fuming nitric acid and 0.325 of silver nitrate, required 4.5 c.c. of 0.112*N*-thiocyanate. $\text{Cl}=16.5$.

$\text{C}_{11}\text{H}_{16}\text{ONCl}$ requires $\text{Cl}=16.6$ per cent.

The substance crystallised from alcohol in flattened, prismatic needles, melting at 69°, and when mixed with cyanodihydrocarvone hydrochloride its melting point was unaltered.

0.402, made up to 25 c.c. with absolute alcohol, at 18°, gave, in a 2-dcm. tube, $\alpha_D + 0.82^\circ$, whence $[\alpha]_D + 25.6^\circ$. Cyanodihydrocarvone hydrochloride has $[\alpha]_D + 25.3^\circ$ at 18° (Trans., 1906, **89**, 1826).

When cyanocarone is dissolved in a saturated solution of hydrogen bromide in glacial acetic acid, and kept for some time, a crystalline substance separates, of which a further amount can be obtained by diluting the acetic acid solution with water; this was collected and crystallised from alcohol:

0.2964, after being heated with fuming nitric acid and 0.2478 of silver nitrate, required 2.68 c.c. of 0.112*N*-thiocyanate. $\text{Br}=30.7$.

$\text{C}_{11}\text{H}_{16}\text{ONBr}$ requires $\text{Br}=31.0$ per cent.

The substance crystallised from alcohol in flattened needles, melting at 85° , and on mixing it with cyanodihydrocarvone hydrobromide, its melting point was unaltered:

0.3546, made up to 25.1 c.c. with absolute alcohol, at 14° , gave, in a 2-dcm. tube, $\alpha_D + 0.72^{\circ}$, whence $[\alpha]_D + 25.5^{\circ}$.

0.3208 of cyanodihydrocarvone hydrobromide, made up to 24.9 c.c. with absolute alcohol, at 14° , gave, in a 2-dcm. tube, $\alpha_D + 0.665^{\circ}$, whence $[\alpha]_D + 25.8^{\circ}$.

Unsaturated Amide.—When cyanocarone is allowed to remain with saturated aqueous hydrogen chloride for some hours, the hydrochloride at first formed slowly dissolves. When the liquid no longer gave the reactions of a nitrile, it was diluted with twice its volume of water, and rendered alkaline with strong ammonia. After cooling, the separated solid was collected and crystallised several times from water:

0.2055 gave 0.5120 CO_2 and 0.1648 H_2O . $\text{C} = 68.0$; $\text{H} = 8.91$.

0.2022 „ 12.8 c.c. N_2 (moist) at 18° and 751 mm. $\text{N} = 7.22$.

$\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 67.7$; $\text{H} = 8.72$; $\text{N} = 7.18$ per cent.

0.2335, made up to 25 c.c. with absolute alcohol, at 18.5° , gave, in a 2-dcm. tube, $\alpha_D + 1.33^{\circ}$, whence $[\alpha]_D + 71.2^{\circ}$.

The amide is readily soluble in hot water or benzene, very soluble in alcohol, acetone, chloroform, or ethyl acetate, and sparingly so in cold water or light petroleum. It crystallises from alcohol or water in small, flattened, white needles, melting at 130° .

It evolves ammonia when boiled with 10 per cent. aqueous sodium hydroxide, reduces permanganate solution immediately in the cold, and decolorises a solution of bromine in acetic acid in presence of sodium acetate.

When heated on the water-bath with concentrated hydrochloric acid, the amide was converted into an acidic substance, which, on dilution, was precipitated as an oil; this was collected, and finally obtained as a solid, which was recrystallised several times from ethyl acetate. It melted at 141 – 142° , and when mixed with β -dihydrocarvonecarboxylic acid its melting point was unaltered. The amide was therefore in all probability an isomeride of the dihydrocarvonecarboxylic amide previously described (Trans., 1906, 89, 958).

Oxidation of Cyanocarone.

An aqueous solution of potassium permanganate oxidises cyanocarone fairly rapidly when heated with it on the water-bath. A solution of 140 grams of potassium permanganate in 3500 c.c. of water was added gradually to a mixture of 20 grams of cyanocarone and 200 c.c. of water. The liquid was filtered from the

precipitated manganese dioxide, evaporated to small bulk, saturated with salt, and extracted with ether twice to remove any unchanged cyanocarone or other neutral material. The liquid was then acidified with hydrochloric acid, and extracted twelve times with ether. The extracted material was freed from volatile material in the usual manner, and was finally obtained as a dark semi-solid mass. This was purified by triturating it with chloroform, and crystallising from a relatively small quantity of chloroform, using a Soxhlet extractor, as it is sparingly soluble in this solvent. After a subsequent crystallisation from water, it was dried at 100° :

0.2065 gave 0.4012 CO_2 and 0.1168 H_2O . $\text{C}=52.98$; $\text{H}=6.28$.

$\text{C}_7\text{H}_{10}\text{O}_4$ requires $\text{C}=53.16$; $\text{H}=6.33$ per cent.

0.1075 required 13.5 c.c. of $N/10$ -sodium hydroxide at -5° for neutralisation, using phenolphthalein as indicator, whence the equivalent = 79.6. A dibasic acid, $\text{C}_7\text{H}_{10}\text{O}_4$, requires equivalent = 79.

The acid crystallised from water in small, white masses, melting at $173-174^{\circ}$. The anhydride, prepared from the acid by means of acetyl chloride, was crystallised from light petroleum, and was found to melt at 55° .

The properties of the acid prove it to be identical with the *cis*-caronic acid prepared by Baeyer and Ipatieff from carone (*Ber.*, 1896, **29**, 2796), and synthesised by Perkin and Thorpe (*Trans.*, 1899, **75**, 48).

The first experiment on the oxidation of cyanocarone was carried out with an aqueous solution of potassium permanganate containing rather more sulphuric acid than that required to combine with the potassium hydroxide which is formed during the oxidation. In this instance, an acid similar in solubility to caronic acid was isolated, which melted, however, at 204° . On titration with sodium hydroxide solution, 0.104 required 6.15 c.c. of 0.1075 N -alkali for neutralisation, using phenolphthalein as indicator, whence equivalent = 157.3. On adding a further 7 c.c. of the alkali and heating for one hour on the water-bath, the excess of alkali required 0.9 c.c. of 0.1003 N -hydrochloric acid for neutralisation, whence the equivalent calculated from the total amount of alkali neutralised = 79.

The data indicate that the substance is the lactone of a saturated hydroxydicarboxylic acid, and probably isomeric with terebic acid.

III.—*The Influence of Water on the Availability of Hydrogen Chloride in Alcoholic Solution.*

By ARTHUR LAPWORTH and JAMES RIDDICK PARTINGTON.

IN recent communications by one of the authors, in part with E. Fitzgerald (Trans., 1908, 93, 2167 *et seq.*), evidence was adduced that during the esterification of a carboxylic acid or the hydrolysis of an ester, as brought about by the catalytic influence of hydrogen chloride, the velocity of reaction was nearly proportional to the concentration of the alcohol and the water respectively, although superficially the velocity of hydrolysis in alcohol or acetone, with a definite concentration of catalyst, appeared to be nearly independent of the concentration of the water over a wide range. The latter effect was attributed to a change in the availability of the catalyst, and was shown to be connected with the observations of Goldschmidt on the retarding influence of water on the esterification of carboxylic acids in alcoholic solution under the influence of mineral acids. Some preliminary experiments were also described which indicated that the phenomena were, as suggested, due in the main to changes in the salt-forming power or availability of the acid acting as catalytic agent, and on measuring the availability of the acid by the use of a weakly basic indicator, it was found that this was greatly altered by small changes in the water-content to an extent which corresponded, in order of magnitude at least, with the simultaneous changes in the velocity of esterification.

Pursuing this train of reasoning, it was demonstrated that the changes in the availability of the acid due to the introduction of water into its solution in alcohol, for example, could not be explained by aid of the view of salt-hydrolysis proposed by Arrhenius, hence, as the power which an acid has of forming complex ions with a weak base of the ammonia type must be proportional to the concentration of free hydrogen ions, other things being equal, it may be inferred that the water acts by diminishing the concentration of the free hydrogen ions if such are present. Consequently water appears to act by uniting with hydrogen ions, as does ammonia, to form complex hydrions. Also, since alcohol and water appear to play similar parts, combination of hydrogen ions with alcohol is probable. With respect to the conception that hydrogen ions unite with water or alcohol, no novelty was claimed, the possibility, even the probability, having been realised by many chemists since the date when the ionic-dissociation hypothesis was first proposed, and especially since the recent development of the oxonium theory.

Goldschmidt and Udby (*Zeitsch. physikal. Chem.*, 1907, 60, 728) had previously used the conception in discussing the kinetics of accelerated esterification, although theirs was an *ad hoc* application of the hypothesis, no attempt having been made by these authors to associate experimentally the anti-catalytic effect of water in esterification processes with alterations in the availability, or salt-forming power, of the acid, and even in applying the conception to the case of a very weak base present in small quantity in an alcoholic solution of hydrogen chloride (*loc. cit.*, p. 731) they picture the hydrated hydrions produced on addition of water as being formed exclusively at the expense of the small amount of salt derived from the weak base (carboxylic acid), which is very far from being the case, as all the salts of weak bases present and the free hydrogen ions, if there, would be diminished in the same proportion.

It is very important to realise that two quite distinct propositions are here involved. The first of these is, that the change in the catalytic activity of a mineral acid in organic solvents, on addition of water, is due to a change in the availability of the mineral acid, and is capable of experimental proof in the manner previously indicated by one of the present authors. The second one concerns the explanation which is to be given of this change in the availability of the mineral acid, and is at present almost wholly hypothetical in character. Fitzgerald and Lapworth, who approached the question from this point of view, were the first to advance the former as a definite proposition, and to indicate the manner in which it might be experimentally established. Goldschmidt and Udby, on the other hand, had previously employed the hypothesis of combination of hydrogen ions with alcohol and water respectively, in explanation of the anti-catalytic effect of water on esterification in alcoholic solution; but as they did not fully realise that the determining factor was the change in the availability of the mineral acid (which naturally depends almost wholly on the alcohol and the water, and only to an almost inappreciable extent on the small quantity of feebly basic carboxylic acid), they applied the hypothesis in an incorrect manner to the calculation of ξ , the concentration of complex hydrions formed by the carboxylic acid (*loc. cit.*, p. 731), entirely overlooking the necessity of taking into consideration the influence of the alcohol used as solvent.

A suggestion made by Goldschmidt and Udby, previously misunderstood by Lapworth, is of great importance in its bearing on the hypothesis of hydrogen ion hydration, and attention may again be drawn to it here. These authors attribute the abnormally large increase in the esterification velocity constant with increasing concentration of catalyst observed in alcohol containing water to the

removal of part of the free water by combination with part of the catalyst (*loc. cit.*, p. 733—735 and 751 *et seq.*; compare also Proc., 1909, 25, 19; Trans., 1908, 93, 2196 and 2197, where the mass of the free water was assumed nearly constant). This explanation (although, in the generalised form given by these authors, it disregards the well-known stimulating effect of anions on the catalytic action of strong acids) is probably correct so far as it applies to the abnormal case where the concentration of the catalyst and the water are comparable, and further investigation of this particular point would appear to be one of the most promising modes of adducing direct evidence as to the correctness or otherwise of the hypothesis of chemical combination between hydrogen ions and solvent.

The present paper contains an account of work done in the expectation of finding that the determining factor in the influence of water on catalysis by mineral acids in alcoholic solution is the availability of the acid for salt formation. The "availability" of an acid may be defined as a function proportional to its capacity for forming complex hydrions with any mon-acid base, and at any moment the concentration of these complex ions is given by $\xi = k.BP$, where k is a constant for the base in the medium used, B the concentration of the free base, and P the "availability" of the acid, or $P = \frac{\xi}{k.B}$. At present it is only feasible to determine the relative values of k for different bases, hence P here has also only a relative magnitude.*

In order to avoid for the present all hypothesis as to the state of a mineral acid in alcoholic solution, an expression for the change in the availability of a mineral acid in absolute alcohol may be developed on the facts adduced by Goldschmidt and by Goldschmidt and Udby.

These authors found that the velocity of esterification in absolute alcoholic solution was proportional to the number of "hydrogen ions," or with a monobasic mineral acid as catalyst, to the product of its concentration and the degree of dissociation. This, however, is also proportional to the concentration of complex hydrions which the acid would yield with a definite concentration of a free mon-acid base, or, in other words, their work affords the proof that in absolute alcohol the velocity of esterification is *ceteris paribus* proportional to the availability of the acid as above defined.

Now Goldschmidt and Udby also find that with a given concentration of mineral acid and carboxylic acid, the velocity of esterification is

* The availability here corresponds with the function $R/V \Sigma M \phi$ developed in a previous paper (*loc. cit.*, p. 2195), where R is the degree of dissociation of the acid; V = the volume which contains one gram-equivalent of acid, M and ϕ corresponding with B and k respectively.

nearly proportional to $\frac{1}{r+w}$, where r is a constant which depends only on the alcohol, and w is the concentration of the water. The contribution which Fitzgerald and Lapworth claim to have made here, is in pointing out that the form of the esterification curve in alcohol departs from the unimolecular type only to the extent that the condition of the catalyst alters, $\frac{1}{r+w}$ being merely a measure of the availability of the catalyst; in other words, the velocity of esterification is proportional to the availability of the catalyst, not only in absolute alcohol, but in moist alcohol too, and $P = \frac{P_0 r}{r+w}$, where P_0 is the availability when $w=0$. It may be noted that with any given state of the mixture of alcohol and water the availability is also proportional to the concentration of the catalyst, hence

$$P = X.c \frac{p.r}{r+w},$$

where c = the concentration of the catalyst, p = its availability when $c=1$ and $w=0$, and X = the degree of dissociation as measured by the electrical conductivity method in a medium having that particular composition. For the highly dilute solutions discussed in the following paragraphs, X is assumed constant.

One of the present authors has already shown that this is the conclusion which must be derived if the hypothesis of combination of the hydrogen ions with the alcohol, the water, and the carboxylic acid be adopted (Trans., 1908, 93, 2195), as the availability must be proportional to the concentration of the free hydrogen ions if these are present.

In order to prove experimentally that this conclusion is the correct one, it is necessary to show that the salt-forming capacity of a very dilute mineral acid varies as $\frac{1}{r+w}$, where r is identical with that calculated from the results of esterification velocity determinations. For the purpose a very weakly basic indicator may be used, and the amount of salt formed with a given concentration of base estimated by colorimetric methods. In practice this is difficult to do, and a somewhat different mode of treatment must be employed, namely, to keep the amount of salt and base nearly constant by varying the concentration of the mineral acid and the water simultaneously. In this case the application of the law of mass action to the definition of availability gives $\xi = k.B.P$, which in terms of the authors' theory is $= kB \frac{p.c.r}{r+w}$, where ξ = the concentration of the complex hydri-
ons,

When ξ and B are constant, then P is also constant, consequently $\frac{c}{r+w}$ is a constant, say K .

It is shown in the practical part of the paper that (1) in these circumstances $\frac{c}{r+w}$ is experimentally nearly constant for salt formation; and (2) with different indicators the value of r is identical with that obtained by observations on the velocity of esterification, within the limits of experimental error, which, it must be admitted, are at present considerable owing to the very small value of r , the measure of the basic affinity of absolute alcohol, and also because of the considerable influence of the merest traces of impurity on the availability of the highly dilute acid which it was necessary to use.

The accurate measurement of the availability of acids in organic media is at present very difficult, owing to circumstances which have already been discussed, and the means which is the most generally applicable, as yet, is that based on determinations of the velocity of esterification, since the basic affinity of alcohols and carboxylic acids is small and less likely to disturb the availability of the highly dilute acid than when indicators, amides, or other definitely basic compounds are introduced; moreover, a carboxylic acid may be chosen to suit a solution of any desired degree of acidity. At the time of the publication of his first paper, and that with E. Fitzgerald, one of us had in view the determination of the availability of acids in various media, simple and mixed, by the electrical method applied in the hydrogen electrode, which, apart from disturbing influences and boundary effects, should theoretically be capable of giving the ratio of the availabilities of an acid in solutions contained in two intercommunicating cells, entirely apart from the reality or otherwise of "free hydrogen ions." Acree has recently drawn attention to the possibility of using the principle of the hydrogen electrode in connexion with experiments on catalysis for the measurement of the concentration of free hydrogen ions (*Amer. Chem. J.*, 1909, **41**, 482). It would be most interesting to obtain confirmation by this means of the "availability formula," $P = \frac{k.c.}{r+w}$, for hydrogen chloride in strong alcohol.

The method should also be applicable to the determination of the relative strengths of bases, weaker than water, in alcoholic and other solutions. Such estimation might also be made by using esterification or tintometric processes, as was previously suggested (*Trans.*, 1908, **93**, 2199), but in connexion with the preliminary numbers previously given, it is necessary to state that the method of determination

employed necessarily leads to quite discrepant values for the affinities of very weak bases, owing to a number of sources of error which were not realised at that time. It was assumed, for example, that most of the base added was in the free state, which is by no means the case when a base such as carbamide competes with alcohol for the acid; moreover, the presence of traces of basic impurities in the material will affect the availability of even a relatively large quantity of an acid when this happens to be one which is feebly ionised, as is the case with trichloroacetic acid in benzene, and our experiments show clearly how difficult it is to be certain that basic impurities in important quantities are absent. With a fuller realisation of these and other points of difficulty it is proposed to undertake the study of affinity constants of some very weak bases in alcoholic solution, in the hope of devising trustworthy methods of measurement.

The hydrogen electrode may also prove useful in investigating the changes in the availability of acids in acetone and in ether. In these, which, as is well known, are poor ionising solvents for hydrogen chloride, acids behave in a remarkable manner towards the first traces of moisture. In pure dry acetone, the first small additions of water do not cause any marked fall in the availability of dissolved hydrogen chloride, although with larger amounts the availability falls off much as it does in alcohol, as is indicated by the numbers given by Fitzgerald and Lapworth for ester hydrolysis and for esterification in moist acetone. In dry ether, again, a very small quantity of water actually causes a decided increase in the availability. These points were first noted during experiments which Mr. Fitzgerald has been conducting on the velocity of esterification in initially dry acetone and ether; here abnormalities were observed in the esterification curve with the former as solvent, while with the latter the curves showed a point of inflexion; tintometric experiments confirmed the conclusion that this was a phenomenon dependent on the availability of the catalyst, and were of interest as adding some weight to the contention that the much discussed changes in the velocity of esterification are due to static causes not connected with the mechanism of reaction except in so far as the availability of the catalyst is concerned.

Experiments on the application of the hydrogen electrode to these questions are now in progress.

EXPERIMENTAL.

The alcohol employed in these determinations was prepared from five distinct specimens, *A*, *B*, *C*, *D*, and *E*. *A* was made from a sample of 96 per cent. spirit by heating it with lime for three days, and subsequently treating the resulting nearly dry alcohol with excess of

calcium. Samples *B*, *C*, *D*, and *E* were made from three different specimens of commercial absolute alcohol. In all cases the last traces of moisture were removed by heating the alcohol with a considerable excess of calcium turnings until a sample of the liquid on addition of water set to a jelly-like mass, indicating that calcium ethoxide was present, and the dried liquid was then directly distilled, the vapour being passed through a trap containing glass wool, the first and last portions rejected, and the middle fraction collected in a dried flask provided with a soda-lime tube to ensure the absence of moisture. The test applied for the presence of calcium ethoxide afforded full proof that the dehydration was as complete as the process was capable of effecting, and further treatment with calcium was obviously superfluous; this conclusion was confirmed by the approximate constancy of the low water value of the four specimens of alcohol obtained in this manner.

Tintometric Experiments.

Aminoazobenzene is an extremely sensitive indicator to hydrogen chloride in absolute alcohol, and was only suitable for concentrations of acid between $N/10,000$ and $N/100,000$, so that errors due to traces of impurities were liable to be unreasonably large. Many other indicators were tried, but the only one having a very decided advantage over aminoazobenzene was an azo-derivative of diphenylamine, the sensitiveness of which was considerably less than that of aminoazobenzene. Further investigation may lead to the discovery of still less basic indicators, more useful than these, for investigations in such solvents as absolute alcohol with higher concentrations of mineral acid.

The principle of the method used throughout has already been discussed; the procedure was to run a definite volume of a solution of alcoholic hydrogen chloride into the absolute alcohol under investigation, partly to discharge the colour by addition of a minute quantity of water, and then to restore the original tint by adding more of the alcoholic hydrogen chloride.

The alcoholic hydrogen chloride and the water were measured from narrow, graduated tubes discharging the liquid from a capillary exit; these tubes had been carefully calibrated, and the errors in reading the small volumes of liquid and those due to alterations in bulk of the original alcohol under investigation were usually within the limits of the experimental error due to other causes. The discrepancies at first were very marked, often leading to differences of 25 per cent. in the "water value" for any specimen of absolute alcohol, and this was finally traced to the effect of the laboratory air with which the

solutions were unavoidably brought into contact during the operation of thoroughly mixing the added acid or water. When the solutions were stirred in the ordinary way with a bent glass rod, it was noticed, especially with the extremely dilute solution of hydrogen chloride employed and with aminoazobenzene as indicator, that very decided changes in the colour occurred in the tintometer, indicating a diminution in the acidity of the solutions. This was due mainly neither to carbon dioxide nor aqueous vapour, as pure dry carbon dioxide had no appreciable influence, and the laboratory air, after being passed through a tube of lime or soda-lime, still produced the same effect. If air dried over sulphuric acid was used to stir the solution, however, the tint did not change, so that the effect was doubtless due to traces of ammonia or some other powerfully basic impurity in the atmosphere. Further, the solutions, if undisturbed or stirred by twisting a spiral glass rod in the solution, did not alter in tint appreciably during the time occupied in an experiment, so that the latter method was finally adopted when using the tubes of a colorimeter to contain the specimens of alcohol.

In all cases 50 c.c. of the specimen of absolute alcohol were used, but three distinct modes of measurement were employed, the temperature of the alcohol in all cases being within two degrees of 25° , except when it is stated otherwise.

(1) The alcohol containing the indicator was contained in a 50 c.c. flask, and alcoholic hydrogen chloride having the same concentration of indicator as the original alcohol was added until the tint was as nearly as possible identical with that in a standard specimen in a similar flask; water was then introduced, and more alcoholic hydrogen chloride to restore as nearly as possible the original tint, this process being repeated several times, the added volume noted in each case, and the water value of the alcohol determined by a graphic method or by the method of least squares.

(2) The alcohol with a trace of indicator was contained in one of the tubes of a colorimeter and tinted by alcoholic hydrogen chloride to nearly the same colour as that of the liquid in the standard tube of the instrument, the exact depth of the standard liquid required to produce a balance being noted. After addition of a measured volume of water, more hydrogen chloride solution was added, and the tint balanced by varying the depth of the standard solution. More hydrogen chloride was then added, the tint again balanced, and so on until a reasonably large number of readings had been made; in this case the depth of the standard solution was found experimentally to be proportional to the hydrogen chloride present when the amount of water was constant, so that the corrections were easily applied.

(3) As in (2), but much more indicator was employed, and the tint

was viewed through a deep blue screen. The depth of the standard liquid was not proportional to the amount of hydrogen chloride in the alcohol, so that separate experiments had to be made to determine the correction formula.

In cases (2) and (3) the water values were at first estimated by a modification of the method of least squares, but this was afterwards abandoned, as they could be obtained graphically within the limits of experimental error.

It will be unnecessary to go into detail in each case, but one or two typical instances of each kind may be given, with the object of indicating the mode of calculation, as well as to show that the formula $P = \frac{kc}{r+w}$ applies here.

TYPE I.

Indicator: Aminoazobenzene. Hydrochloric acid = $N/100$ nearly.

W = water present in c.c.

H = volume of alcoholic hydrogen chloride added in c.c.

A = total volume of alcohol.

$h = \frac{H}{A} A_0$, or quantity of acid per 50 c.c. of alcohol.

R = the water value, in grams, of 50 c.c. of the alcohol used.

$W' = \frac{50W}{A}$, or the amount of water per 50 c.c. of alcohol.

$C = \frac{h}{W' + R}$.

W .	H .	A .	h .	W' .	C .
0.00	1.00	51.0	1.00	0.000	10.3
0.09	2.00	52.0	1.96	0.086	10.7
0.18	2.83	52.8	2.73	0.171	10.2
0.36	4.70	54.7	4.31	0.329	10.1
0.72	8.40	58.4	7.34	0.616	10.3

R = water value per 50 c.c. of the alcohol at $25^\circ = 0.097$ gram, whence $r = 10.8$.

For the applicability of the formula $P = \frac{kc}{r+w}$ (see above), the value of C should be constant.

TYPE III.

Indicator: *p*-Tolueneazodiphenylamine, used with blue screen. Strength of alcoholic hydrogen chloride added was between $N/5$ and $N/10$. (In these cases no correction was needed for the relatively small volume of alcoholic hydrogen chloride added, which did not amount to more than 2 per cent. of the total volume of alcohol used.)

W = c.c. of water present (in 50 c.c. of alcohol).

H = volume of alcoholic hydrogen chloride in c.c.

l = height of adjustable column of standard liquid in cm.

A series of measurements showed that under the conditions and within the limits used, the product $H \times \left(\frac{1}{l} - 0.04\right)$ was constant with absolute alcohol, or with alcohol containing any fixed concentration of water. Hence this product was equal to $H_o \times \left(\frac{1}{l_o} - 0.04\right)$, where H_o is the volume of alcoholic hydrogen chloride which would be necessary to produce any standard tint corresponding with the fixed height, l_o .

As $\left(\frac{1}{l_o} - 0.04\right)$ is constant, then for any two observations the relation between the amounts of acid H_o and H_o' required to produce

a standard tint was given by $\frac{H_o}{H_o'} = \frac{H \times \left(\frac{1}{l} - 0.04\right)}{H \times \left(\frac{1}{l'} - 0.04\right)}$; or the product

$H \times \left(\frac{1}{l} - 0.04\right)$ is proportional to the amount of hydrogen chloride required to produce any definite standard tint with a fixed water-content.

Two instances are given. The first to indicate the applicability of the foregoing correction formula, and the second to demonstrate that the formula $H_o = (r + w) \times \text{a constant}$ is applicable when the water varies in amount, and, therefore, $P = \frac{k}{r + w}$ when the amount of hydrogen chloride is constant (compare p. 23).

EXAMPLE I.

W .	l .	B .	H .	$H \times B$.	C .
0.0	7.85	0.0876	0.25	0.0219	2.38
0.0	8.40	0.0790	0.28	0.0221	2.40
0.0	8.95	0.0717	0.30	0.02151	2.33
0.074	8.35	0.0798	0.50	0.0399	2.40
0.074	8.70	0.0749	0.53	0.0397	2.39
0.074	8.95	0.0717	0.55	0.0394	2.37
0.221	8.10	0.0835	0.90	0.07515	2.40
0.221	8.55	0.0770	0.97	0.0748	2.39
0.221	8.85	0.0730	1.04	0.0759	2.42

The water value, R , of 50 c.c. of the alcohol used was = 0.092 gram. The column headed B contains the values of $\left(\frac{1}{l} - 0.04\right)$, and C , those of $\frac{H \times B}{R + W}$.

The applicability of the correction formula $H \times \left(\frac{1}{l} - 0.04\right)$ is shown by the close agreement between the bracketed values of $H \times B$.

The applicability of the availability formula $P = k \frac{c}{r+w}$ is shown by the approximate constancy in the values of C throughout.

EXAMPLE II.

<i>W.</i>	<i>l.</i>	<i>B.</i>	<i>H.</i>	<i>H</i> × <i>B.</i>	<i>C.</i>
0.0	8.40	0.0790	0.165	0.01304	1.37
0.0	8.79	0.0738	0.18	0.0133	1.40
0.0	9.62	0.0641	0.20	0.01282	1.35
0.0552	8.73	0.0745	0.29	0.0216	1.44
0.0552	9.03	0.0707	0.30	0.0212	1.41
0.1935	7.89	0.0867	0.46	0.0399	1.38
0.2655	7.55	0.0925	0.53	0.0490	1.36
0.3519	7.62	0.0912	0.68	0.0620	1.39
0.4329	7.87	0.0871	0.85	0.0740	1.40
0.486	8.47	0.0781	1.01	0.0789	1.36

R, or water value, = 0.095 gram for 50 c.c. of the absolute alcohol, whence $r = 0.106$ (or 1 litre of the absolute alcohol used was equivalent to 0.106 gram-molecules of water at 25°).

Esterification Experiments.

For the determination of the water value of the alcohol by the esterification process, purified phenylacetic acid dried in a vacuum over sulphuric acid was employed in all cases. The flasks employed were subjected to the action of a current of steam for a quarter of an hour, and then carefully dried before each experiment. The dry acid was only roughly measured, but the water in each case was weighed. From each sample of alcohol a solution of hydrogen chloride of about $N/10$ strength was prepared by passing the dried gas into a portion of the specimen, care being taken to exclude moisture. The alcoholic solutions before admixture were all first heated to the temperature of the thermostat, and the moment when the reaction commenced was noted. One or two titrations were always made near the commencement of the reaction for the purpose of obtaining the true initial titre by extrapolation, as this value was required for a knowledge of the exact amount of water present at any stage. The titre of the hydrogen chloride present at the beginning and end of each experiment was taken, using $N/100$ -silver nitrate, thus definitely ensuring constancy in the amount of catalyst.

Two flasks were always examined simultaneously, one containing the initially dry alcohol, and the other, alcohol containing initially a weighed quantity of water.

The intermediate values of the constants being the most trustworthy, the approximate water value of the alcohol is best gauged by comparing the intermediate values of the constants obtained for the two flasks. That is to say, the value of r was not ascertained by the reference to

the constancy of the value for any one experiment, but by comparing the numbers obtained in the two experiments.

This method commends itself as the best, since the more trustworthy values for the velocity are of course those calculated from the time when the change has become steady to a point not far from half way towards the end. All the titres, y , are corrected for the hydrochloric acid present.

The bracketed values of the titre y for $T = 0$ were obtained by graphic extrapolation from the first few observations, for which no constant was calculated. R was calculated throughout from the formula corresponding with that used by Goldschmidt and Udby as

$$-\frac{dy}{dt} = kc \cdot \frac{y}{R + W + y_0 - y}$$

when the concentration of the catalyst is constant,

whence
$$kc = \frac{(R + W + y_0)(\log_e y_1 - \log_e y) - (y_1 - y)}{T - T_1},$$

where R = the water equivalent of 10 c.c. of the alcohol used in $N/10$ c.c.

W = the equivalent of the initially added water.

y = the titre of 10 c.c. of the solution at the time T .

y_0 = initial titre [bracketed value] of 10 c.c. of the solution calculated by extrapolation.

y_1 = the first titre actually made at the time T_1 .

The time is given in minutes, and the titres are c.c. of $N/10$ -alkali required to neutralise the free phenylacetic acid present in 10 c.c. of the solution investigated.

(r in all cases in this paper refers to the water equivalent in gram-molecules of one litre of alcohol.)

Esterification Results for Specimen A.

Each flask had a capacity of 100 c.c. Amount of solution used for each titre = 10 c.c. Time in minutes. Titre given in c.c. of $N/10$ -sodium hydroxide. Hydrochloric acid during reaction was $0.0195N$, nearly.

Flask I.—No water.

T .	y .	kc , assuming			
		$r=0.15$.	$r=0.11$.	$r=0.10$.	$r=0.09$.
[0	9.93]	—	—	—	—
7	9.50	—	—	—	—
29	8.32	—	—	—	—
42	7.63	—	—	—	—
68	6.47	10.74	8.23	7.61	6.95
137	4.44	10.68	8.36	7.77	7.17
212	3.09	10.51	8.31	7.80	7.24
287	2.18	10.49	8.38	7.89	7.34
Mean.....		10.61	8.32	7.77	7.18

Flask II.—Water = 0.36 gram.

<i>T.</i>	<i>y.</i>	<i>kc</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0	20.2]	—	—	—	—
15	19.50	—	—	—	—
30	18.81	—	—	—	—
69	17.10	8.96	7.87	7.76	7.50
138	14.52	9.16	8.21	7.96	7.70
216	12.30	9.08	8.11	7.91	7.68
446	7.91	8.86	8.04	7.82	7.59
Mean.....		9.02	8.06	7.87	7.62

The value of *r* evidently lies between 0.10 and 0.11.

A series of tintometric experiments for this specimen of absolute alcohol gave *r* = (i) 0.105, 0.101, 0.105.

(ii) 0.093, 0.101.

(iii) 0.105, 0.101, 0.101, 0.095.

Series B.—Each flask had a capacity of 50 c.c. Amount of solution used for each titration = 10 c.c. Time in minutes. Titre given in c.c. *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0140*N*, nearly.

Flask I.—With no water.

<i>T.</i>	<i>y.</i>	<i>kc</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0	11.43]	—	—	—	—
12	10.80	—	—	—	—
98	7.52	7.32	5.63	5.21	4.77
220	5.02	6.95	5.48	5.11	4.73
303	3.75	7.17	5.73	5.36	5.00
Mean.....		7.15	5.61	5.23	4.83

Flask II.—With 0.18 gram of water.

<i>T.</i>	<i>y.</i>	<i>kc</i> , assuming			
		<i>r</i> = 0.15.	<i>r</i> = 0.11.	<i>r</i> = 0.10.	<i>r</i> = 0.09.
[0	10.50]	—	—	—	—
10	10.30	—	—	—	—
95	8.88	6.28	5.57	5.40	5.23
205	7.30	6.49	5.77	5.61	5.43
300	6.26	6.41	5.74	5.56	5.39
Mean.....		6.39	5.69	5.52	5.35

The value of *r* evidently lies just above 0.11.

Tintometric measurements gave *r* = { (ii) 0.098, 0.106, 0.108.
(iii) 0.108, 0.098, 0.100.

Series C.—Each flask had a capacity of 50 c.c. Amount of solution used for titration = 10 c.c. Time in minutes. Titre given in c.c. of

N/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0182*N*.

Flask I.—No water.

<i>T</i> .	<i>y</i> .	<i>kc</i> , assuming			
		<i>r</i> =0.15.	<i>r</i> =0.11.	<i>r</i> =0.10.	<i>r</i> =0.09.
[0	9.59]	—	—	—	—
11	8.83	—	—	—	—
27	7.93	10.81	8.22	7.53	6.83
96	5.36	10.34	7.98	7.42	6.84
186	3.48	10.00	7.90	7.36	6.83
Mean.....		10.38	8.03	7.44	6.83

Flask II.—Water = 0.1430 gram.

<i>T</i> .	<i>y</i> .	<i>kc</i> , assuming			
		<i>r</i> =0.15.	<i>r</i> =0.11.	<i>r</i> =0.10.	<i>r</i> =0.09.
[0	12.70]	—	—	—	—
22	11.73	—	—	—	—
67	10.35	9.04	7.93	7.64	7.38
260	6.43	8.80	7.79	7.54	7.28
487	3.85	8.76	7.77	7.50	7.27
Mean.....		8.87	7.83	7.56	7.31

From above, *r* is evidently between 0.10 and 0.11.

Tintometric experiments gave = *r* { (ii) 0.098, 0.095.
(iii) 0.101, 0.105.

Series D.—Each flask had a capacity of 100 c.c. Amount of solution titrated = 10 c.c. Time in minutes. Titres in terms of *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0278 *N*, nearly.

Flask I.—No water. Flask II.—Water = 0.10 gram.

Flask III.—Water = 0.20 gram.

<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).	<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).	<i>T</i> .	<i>y</i> .	<i>kc</i> (<i>r</i> =0.10).
[0	13.33]	—	[0	13.33]	—	[0	13.33]	—
14	12.05	—	18	12.30	—	21	12.47	—
42	9.71	—	44	10.69	—	46	11.08	—
66	8.19	0.987	71	9.16	0.986	73	9.91	0.987
126	5.65	1.006	131	6.83	0.992	131	7.73	1.001
221	3.48	0.985	225	4.50	1.001	227	5.43	1.007

Tintometric experiments gave *r* = 0.09 and 0.11 by (i).

Series E.—Each flask had a capacity of 100 c.c. Amount of solution titrated = 10 c.c. Time in minutes. Titres in terms of *N*/10-sodium hydroxide. Hydrochloric acid during reaction was 0.0201*N*, nearly.

Flask I.—No water.

Flask II.—Water = 0.197 gram.

<i>T.</i>	<i>y.</i>	<i>kc</i> ($r=0.10$).
[0	12.5]	—
11	11.5	—
25	10.4	—
116	6.25	0.805
120	6.15	0.803
272	3.16	0.792
372	2.12	0.793
Mean.....		0.798

<i>T.</i>	<i>y.</i>	<i>kc</i> ($r=0.10$).
[0	12.7]	—
20	11.75	—
50	10.45	—
129	8.18	0.787
280	5.15	0.815
369	4.05	0.805
Mean.....		0.802

whence r is almost exactly 0.10.

Tintometric experiments gave $r = \begin{cases} \text{(ii)} & 0.090, 0.089. \\ \text{(iii)} & 0.095, 0.098, 0.090. \end{cases}$

The apparent discrepancy between the values of r found, as above, and the value 0.15 used by Goldschmidt and Udby is apparently due mainly to the circumstance that they calculated the value for higher concentrations of catalyst. A comparison of the numbers for the velocity of reaction at low concentrations indicates that the alcohol used by these authors was probably as dry as that used in the experiments detailed in the present paper.

Summary.

(i) The "availability" of a *very dilute solution of hydrogen chloride* in moist alcohol is nearly an inverse linear function of the amount of water present for quantities of water not exceeding a concentration of $N/2$.

(ii) The effect is a static one, and there is no reason to believe that the anti-catalytic effect of water is due to any other cause than a change in the availability of the acid; it is not, for instance, to any appreciable extent the result of any influences, such as increase in viscosity, tending to lower the measured velocity of reaction (on this point compare, however, S. F. Acree, *Amer. Chem. J.*, 1909, 41, 471), nor is it the result of ester hydrolysis.

(iii) The availability within the above range may be very nearly represented by $c \frac{k}{r+w}$, where c = concentration of the hydrogen chloride, k being a constant, w the concentration of water present, r being the water equivalent of the alcohol present.

(iv) r is a constant which depends on the alcohol (as Goldschmidt and Udby have demonstrated in the case of esterification), but, within the limits of experimental error, is the same whether the availability of the acid be measured by means of esterification velocities or by estimating the amount of the salt which the acid can form with a weak non-acid base.

(v) For absolute alcohol dried over excess of calcium, r is about 0.10 for very low concentrations of hydrogen chloride at 25° ; thus, at this temperature, the availability of hydrochloric acid in absolute alcohol is lowered 50 per cent. by the addition of 1.8 grams of water per litre of alcohol.

(vi) If any free hydrogen ions exist in solutions of acids in water or alcohol, an assumption for which there is at present no direct evidence, then for small changes in the composition of the mixture of water and alcohol it may be concluded that the concentration of these is a measure of the availability of the acid.

(vii) The fundamental difference between the view of Goldschmidt and Uddy and that of Fitzgerald and Lapworth revolves on the point that the first-named workers, although realising that the catalyst is mostly shared between the alcohol and the water, neglected to consider the change in the availability of the catalyst when water is added to its alcoholic solution, and consequently they formed an incorrect conception of the manner in which water would affect the equilibrium between a dissolved weak base and its salt.

The authors desire to state that most of the cost of this investigation was defrayed by a grant from the Government Grant Research Fund of the Royal Society, and for this they wish to express their indebtedness.

SCHUNCK LABORATORY,
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IV.—*Organic Derivatives of Antimony. Part I.* *Tricamphorylstibine Chloride and Triphenylstibine* *Hydroxynitrate and Hydroxysulphate.*

By GILBERT T. MORGAN, FRANCES M. G. MICKLETHWAIT, and
GEORGE STAFFORD WHITBY, B.Sc., A.R.C.S.

A COMPARATIVE study of the interactions taking place between sodium camphor and the trichlorides of phosphorus, arsenic, and antimony has shown that in the case of the arsenic compound the principal products are dicamphorylarsinic and tricamphorylarsinic acids (Trans., 1908, **23**, 2144; 1909, **95**, 1473). The experiments with phosphorus trichloride are still in progress; the present communication deals with the case of antimony trichloride.

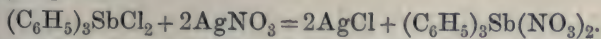
The interaction of sodium camphor and antimony trichloride in

dry toluene does not lead to the production of any substances soluble in aqueous alkali hydroxides or carbonates. The only product definitely isolated and identified is *tricamphorylstibine chloride*, $(C_{10}H_{15}O)_3SbCl_2$. This substance undergoes destructive hydrolysis so readily that the resulting tricamphorylstibine oxide, $(C_{10}H_{15}O)_3SbO$, is always more or less contaminated with hydrated antimonious oxide arising from the decomposition of the chloride into hydrochloric and antimonious acids and camphor.

As one object of this research was to obtain an organic derivative of antimony sufficiently stable and soluble for employment as a therapeutic agent, attention was now directed to triphenylstibine chloride, $(C_6H_5)_3SbCl_2$, obtained by Michaelis and Reese by the interaction of chlorobenzene, antimony trichloride, and sodium (*Annalen*, 1886, **233**, 43).

As these investigators have stated that this aromatic antimony derivative is possessed of considerable stability, attempts were made to convert this substance into compounds dissolving more readily in aqueous solutions.

When treated with alcoholic silver nitrate, triphenylstibine chloride loses its chlorine quantitatively in accordance with the following equation:



The triphenylstibine nitrate is not stable under these conditions, and undergoes partial hydrolysis into a definitely crystalline substance, *triphenylstibine hydroxynitrate*, $(C_6H_5)_3Sb(OH) \cdot NO_3$, which may be recrystallised from hot water without further hydrolysis. In connexion with the formation of this substance, it is of interest to note that Michaelis and Reese describe a triphenylstibine nitrate, prepared by dissolving triphenylstibine in hot fuming nitric acid (*loc. cit.*, p. 52), which is stated to be insoluble in water, but crystallisable from alcohol.

The substitution of silver sulphate for silver nitrate in the foregoing reaction leads to the production of the corresponding *triphenylstibine hydroxysulphate*, $(C_6H_5)_3Sb(OH) \cdot SO_4 \cdot Sb(OH)(C_6H_5)_3$, which is less soluble in water than the hydroxynitrate.

EXPERIMENTAL.

Tricamphorylstibine Chloride.—On adding a toluene solution of antimony trichloride to sodium camphor suspended in the same medium, considerable heat was generated, and a bulky precipitate was produced. The mixture was warmed on the water-bath and left for a few days, after which it was treated with water, when a white precipitate of antimony oxides separated. The toluene

solution which drained from this precipitate was distilled in steam, and the residue extracted with benzene. From the concentrated benzene extract, a substance separated in colourless, ice-like crystals, this separation being promoted by the addition of light petroleum. After repeated crystallisation from benzene, the product melted and decomposed at 244° , although when rapidly heated it sometimes remained unchanged at $247-248^{\circ}$:

0.1314 gave 0.2660 CO_2 and 0.0840 H_2O . $\text{C} = 55.21$; $\text{H} = 7.10$.
 0.1830 „ 0.3706 CO_2 „ 0.1116 H_2O . $\text{C} = 55.22$; $\text{H} = 6.77$.
 0.2235 „ 0.0591 Sb_2S_3 . $\text{Sb} = 18.88$.
 0.2483 „ 0.1106 AgCl . $\text{Cl} = 11.02$.
 $\text{C}_{30}\text{H}_{45}\text{O}_3\text{ClSb}$ requires $\text{C} = 55.90$; $\text{H} = 7.0$; $\text{Sb} = 18.63$;
 $\text{Cl} = 11.02$ per cent.

0.3120, in 25 c.c. chloroform, at 20° , gave $\alpha_D + 9.17^{\circ}$, whence $[\alpha]_D = 367.3^{\circ}$.

Tricamphorylstibine chloride dissolves only sparingly in alcohol, and is insoluble in water. In acid solutions it is fairly stable, and may be boiled with 2*N*-hydrochloric acid without decomposition. On warming with 2*N*-sodium hydroxide, the chloride was readily hydrolysed into antimonie and hydrochloric acids and camphor. Destructive hydrolysis occurred on warming the chloride with aqueous sodium hydrogen carbonate at 55° , and continued heating with dilute ammonia led to the liberation of camphor. A similar decomposition took place when the chloride was digested with alcoholic silver nitrate.

Triphenylstibine Hydroxynitrate.—0.621 Gram of triphenylstibine chloride gave 0.419 gram of silver chloride (the calculated amount being 0.421 gram) on warming with two molecular proportions of silver nitrate in alcoholic solution. The filtrate, on concentration, furnished white crystals, which, on analysis, gave numbers corresponding with the partial hydrolysis of the initially formed dinitrate. This hydrolysis was brought to a definite end-point by dissolving the white crystals in boiling water, for, on cooling, the hydroxynitrate separated in lustrous, colourless leaflets, softening at 220° , and melting to a yellow liquid at $224-225^{\circ}$.

When carrying out the process on a larger scale, any slight excess of silver retained in the solution was precipitated by the addition of sodium chloride. The presence of excess of this salt in the filtrate promoted the crystallisation of the hydroxynitrate, the precipitation, under these conditions, being almost complete:

0.2691 gave 0.4932 CO_2 and 0.0942 H_2O . $\text{C} = 50.00$; $\text{H} = 3.80$.
 0.3765 „ 0.1461 Sb_2S_3 . $\text{Sb} = 27.72$.

0.3300 gave 9.6 c.c. N_2 at 24° and 759 mm. $N=3.19$.

$C_{18}H_{16}O_4NSb$ requires $C=50.23$; $H=3.72$; $Sb=27.9$;
 $N=3.26$ per cent.

Triphenylstibine hydroxynitrate is almost insoluble in cold water, but dissolves very readily in alcohol, giving rise to a solution which can be diluted with water very considerably without any deposition of the hydroxynitrate taking place. When reduced with Devarda's alloy (Al-Cu couple) in the presence of alkali, triphenylstibine is produced, and the whole of the nitrogen is eliminated as ammonia. An estimation of nitrogen by this method gave 3.62, the calculated value being 3.19 per cent.

Triphenylstibine hydroxysulphate was prepared by adding an alcoholic solution of triphenylstibine chloride (1 mol.) to a boiling aqueous solution of silver sulphate (2 mols.). The filtrate from the silver chloride was concentrated to remove the alcohol, when the hydroxysulphate separated in colourless nodular crystals, the solution being then distinctly acid, owing to the liberation of sulphuric acid:

0.2602 gave 0.0761 $BaSO_4$. $S=4.01$.

$C_{36}H_{32}O_6SSb_2$ requires $S=3.84$ per cent.

The hydroxysulphate is almost insoluble in cold water; it dissolves in cold concentrated sulphuric acid, and remains in solution after considerable dilution with water, this increase in solubility indicating its conversion into the normal sulphate.

Triphenylstibine hydroxysulphate melts and decomposes at 252° .

Triphenylstibine hydroxychloride was produced by adding an alcoholic solution of triphenylstibine chloride to a large volume of boiling water and evaporating until crystallisation began. The crystalline deposit, when dried and dissolved in benzene, separated from this solvent in transparent, lustrous, colourless spicules, melting at 218° :

0.2982 gave 0.1240 Sb_2S_3 . $Sb=29.70$.

$C_{18}H_{16}OClSb$ requires $Sb=29.73$ per cent.

The authors desire to express their thanks to the Government Grant Committee of the Royal Society for a grant, which has partly defrayed the expenses of this investigation.

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V.—*Experiments on Substituted Allenecarboxylic Acids. Part I.*

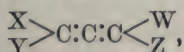
By ARTHUR LAPWORTH and ELKAN WECHSLER.

SINCE the appearance of Thiele's papers on the conjugation of unsaturated linkings, an increasing amount of attention has been paid to the question of the mutual influence of points of unsaturation within the molecule, and to the manner in which this influence varies with the relative disposition of these centres of activity.

Thiele has pointed out that the stability of the conjugated system of atoms, $X:Y:Z:W$, is, as a rule, much greater than that of isomeric systems in which the ethylenic and single linkings are not arranged alternately. Such a system therefore has an abnormally small residual affinity, and abnormalities in chemical and physical behaviour are naturally associated with the presence of this structure. It would appear, a priori, not improbable that the system $X:Y:Z$ represents that with the greatest residual affinity; it might therefore be anticipated that any abnormalities displayed by substances containing it would, for the most part, be opposite in sense to those shown by compounds containing the conjugated system; the resulting reactivity of the complex is doubtless the reason why so few allene derivatives have as yet been isolated, and is the most obvious explanation of the circumstance. Instability might be expected to demonstrate itself in isomeric change of the substance at the moment of its formation into an acetylene derivative, or into the isomeric compound with the bonds in the conjugated position, where this is possible, or by the rapid absorption of water or other available reagent. The great activity of the ketens $R_2C:C:O$ is suggestive in connexion with this point. In order that an allene derivative should possess a comparatively high degree of stability, it seemed desirable that isomeric change by the migration of double linkings should, as far as possible, be obviated, and, further, that the residual affinity of the complex should be made as low as possible by associating each of the ethylenic linkings with another centre of unsaturation, so as to introduce the effect of conjugation. Thus it was to be anticipated that the system $C:C:C:C:C$ would have a degree of permanence intermediate between that of a conjugated and a simple allene system.

Some of the effects of conjugation are noticed when an aromatic nucleus or a carbonyl group is directly attached to two doubly

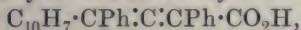
linked atoms, and a quite definite degree of stability might be anticipated in the case of an allene derivative,



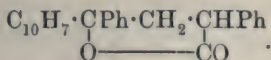
in which X, Y, W, Z are all either aromatic nuclei or carbonyl groups.

With the view of ascertaining how far these extensions of the conceptions of Thiele would apply to such a case, it was decided to attempt the preparation of a substance of this type. Such a substance possesses an interest which is enhanced by the fact that its molecule is built on one of the types shown by van't Hoff to be theoretically capable of exhibiting the phenomenon of enantiomorphous isomerism associated with optical activity, in spite of the circumstance that no asymmetric atom in the strict sense is present. The latter property, it may be pointed out, is not restricted to the case in which the four groups X, Y, W, and Z are all different, but requires only the condition that X is not identical with Y, and W is not the same as Z.

The first substance which the authors sought to prepare was $\alpha\gamma$ -diphenyl- γ -1-naphthylallene- α -carboxylic acid,



in which all of those conditions are realised. The method adopted was to proceed from the ester of β -benzoyl- α -phenylpropionic acid, $\text{CH}_2\text{Bz} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$. This was allowed to react with magnesium α -naphthyl bromide, and, under the conditions finally imposed, gave the lactone:



In the next stage of the process, the lactone was heated with phosphorus pentachloride on the water-bath, and the product poured into absolute alcohol in the anticipation that the chloro-ester would thus be produced, but it was noticed that during this treatment much hydrogen chloride was evolved, indicating that either an unsaturated compound was in process of formation, or that replacement of hydrogen by chlorine was taking place, but the product, however, behaved as a saturated compound. The gummy ester yielded no crystalline material, even after boiling with tertiary bases with the object of removing the hydrogen chloride, but finally it was discovered that, by using rather more than two molecular proportions of phosphorus pentachloride, the product, treated as indicated above, gave a moderately good yield of a crystalline ester, free from chlorine.

The new substance was for a long time thought to be the unsaturated ester, $\text{C}_{10}\text{H}_7 \cdot \text{CPh} : \text{CH} \cdot \text{CHPh} \cdot \text{CO}_2\text{Et}$, formed by the

removal of the elements of hydrogen chloride from the chloro-ester above depicted, but the analyses of the pure compound and all its derivatives gave numbers for the hydrogen content which were decidedly too low, and the analytical evidence shows that the molecules contain two hydrogen atoms less than required by substances directly derived from one having the above formula.

The phosphorus pentachloride had therefore replaced hydrogen as well as oxygen by chlorine, and doubtless at the α -position with respect to the carbonyl group, so that the necessity for using at least two molecular proportions of this agent was accounted for.*

In view of the concordance of all the analytical results and in spite of certain abnormal properties of some of the derivatives, we have no hesitation in affirming our view that the crystalline ester has a formula containing two hydrogen atoms less than the number shown in the above structure, and may be regarded as being formed by the removal of two molecules of hydrogen chloride from a dichloro-ester or an unsaturated monochloro-ester.

For a long time the authors were convinced that they had to deal here with phenyldinaphthylallenecarboxylic acid, with the synthesis of which they had concerned themselves, but in view of a paper by Vorländer and Siebert (*Ber.*, 1906, **39**, 1024), to which their attention was afterwards directed, their confidence is not complete. The communication referred to contains an account of tetraphenylallene, which is formed, instead of tetraphenylacetone, when barium diphenylacetate is heated; the ease with which the allene grouping is formed in this instance illustrates again, in a clear manner, the effect of the aromatic nucleus from the point of view discussed in the previous pages. Tetraphenylallene, like some of the unsaturated compounds, but unlike the acid described in the present paper, is stable towards permanganate (in acetone solution), but is slowly oxidised by chromic acid; on treatment with acids, it yields an isomeric hydrocarbon, in which the allene structure is apparently not present. Further the original hydrocarbon on bromination yields a monobromo-derivative of the isomeric hydrocarbon.

Having regard to the characters and mode of formation of all the substances here described and the work of Vorländer and Siebert, the most probable view seems to be that the acid itself has the allene structure, but that its lactone and the bromo-

* The direct replacement of hydrogen by chlorine when phosphorus pentachloride is used at a temperature at 100° is certainly unusual. Autenrieth, however, found that anisole was chlorinated by this agent at $30-70^{\circ}$ (*Arch. Pharm.*, 1895, **233**, 31), and Titherley and Hicks noticed that phosphorus pentachloride replaces hydrogen by chlorine when it is heated with phenylbenzometoxazine in chloroform solution at 60° (*Trans.*, 1909, **95**, 912),

derivative are perhaps genetically related to the isomeride of tetraphenylallene.

The acid in question is very readily altered by treatment in alkaline solution with sodium amalgam, and although the reduction products have not yet been obtained in crystalline form, this property indicates that the acid is probably an $\alpha\beta$ -unsaturated acid.

It very readily yields a lactone on treatment with mineral acids, so that it is probably a $\beta\gamma$ -unsaturated acid. Further, the lactone thus obtained is not identical with the saturated lactone from which the acid had originally been prepared, nor does it contain a detectable quantity of this very characteristic substance.

On the other hand, the acid and its ester only absorb one molecular proportion of bromine, yielding a monobromo-lactone; this exhibits great stability, and resists for some time the action of hot permanganate solution.

The acid unites with ether to form a very stable, crystalline substance, from which the ether is only removed with difficulty even at 100°. The salts which the acid forms with bases, however, show little or no tendency to crystallise; the salts with alkalis behave as soaps, and the compounds of the acid with all the organic bases and alkaloids experimented with, piperidine excepted, did not yield any trace of crystalline salt.

Other methods applicable for resolving acids into their enantiomorphous constituents were tried, but in all cases without definite result.

The results are presented in their present form, as the authors are no longer able to work in collaboration.

EXPERIMENTAL.

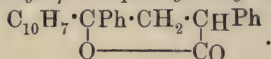
In preparing the β -benzoyl- α -phenylpropionitrile required for the investigation, the process described by Hann and Lapworth (Trans., 1904, 85, 1358) was found to be tedious and wasteful of alcohol when large quantities of material were dealt with. After a considerable number of experiments, the following modified process was found to give excellent results.

A solution of benzylideneacetophenone (23.4 grams) in 120 c.c. of 96 per cent. alcohol and 8.0 c.c. of glacial acetic acid was warmed to 50°, and into this was then introduced, by means of a test-tube drawn out at the end to a coarse capillary which rested on the bottom of the flask, a solution of potassium cyanide (15 grams) in 25 c.c. of water. The temperature was maintained at 50—55° for a further fifteen minutes, when crystals of the nitrile were added, and the vessel was then cooled by a stream of cold water. The

deposited solid, which was obtained in nearly theoretical quantity, was purified by crystallisation from alcohol.

The following modified process was used in hydrolysing the nitrile. Ten grams of the finely powdered compound were shaken with a mixture of 50 grams of sulphuric acid and 25 grams of water, at the temperature of the water-bath, until dissolved, and the whole was subsequently allowed to remain on the bath for several hours. After cooling, the cake of impure acid formed was separated, washed, and purified as before (*loc. cit.*, p. 1361). The preparation of the ethyl ester was effected by warming the dry acid with half its weight of sulphuric acid and ten times its weight of alcohol for several hours, the liquid being then poured into a large bulk of water, which was afterwards shaken with an equal bulk of light petroleum. After filtration, the fluids separate rapidly, and the petroleum solution, after being washed with dilute sodium carbonate solution, dried, and evaporated, deposits the ester in magnificent crystals.

αγ-Diphenyl-γ-1-naphthylbutyrolactone,



Magnesium α -naphthyl bromide in ethereal solution was prepared in the usual manner, and added to a solution containing one molecular proportion of ethyl β -benzoyl- α -phenylpropionate in about twenty times its weight of benzene. The solution was not cooled during this process, as it was found that a much better yield of the desired product was thus obtained, owing probably to the fact that the solution, if cooled, deposited a viscid oil, which tended to carry down with it much of the unaltered ester. At the end of the operation the solution was freed from magnesium compounds in the usual manner, and the ether and benzene were afterwards removed by the use of a current of steam. The residual viscid mass was separated from the water and dissolved in hot acetone, the crystals which separated on cooling being removed at the end of twenty-four hours, and recrystallised fresh from a mixture of acetone and alcohol, and finally from glacial acetic acid:

0.4812 gave 1.5022 CO_2 and 0.2443 H_2O . $\text{C}=85.14$; $\text{H}=5.64$.

$\text{C}_{26}\text{H}_{20}\text{O}_2$ requires $\text{C}=85.71$; $\text{H}=5.49$ per cent.

The substance is insoluble in water, only very sparingly soluble in boiling methyl and ethyl alcohols, ether, or light petroleum; it is fairly soluble in carbon disulphide, and readily so in glacial acetic acid, acetone, chloroform, carbon tetrachloride, or benzene. It separates from acetone in colourless, transparent prisms, containing acetone of crystallisation, melting at about

90° (when rapidly heated) to a colourless liquid, from which the acetone rapidly evaporates, leaving a white, crystalline solid, which, on further heating, melts at 166°. The substance, when obtained by crystallisation from hot glacial acetic acid, is free from acetone and melts at 166°.

This lactone dissolves very slowly in boiling aqueous alkalis, but more rapidly in the presence of alcohol. On evaporating the solution or on adding sodium hydroxide, the sodium salt separates as a voluminous, white, gelatinous mass. The cold aqueous solution of the sodium salt, on addition of hydrochloric acid, deposits the hydroxy-acid as a white, amorphous precipitate; this may be extracted with ether, in which it dissolves readily. A crystalline substance rapidly separates when the ethereal extract is allowed to evaporate, but this, on examination, is found to be identical with the original lactone. Owing to the ease with which lactone formation takes place, it is probably not possible to isolate the free acid in a state of purity; the substance precipitated from the solution of the sodium salt consists, nevertheless, of the hydroxy-acid and not of the lactone, for the freshly precipitated substance is readily soluble in dilute aqueous sodium carbonate and in ether, whereas the lactone is insoluble in the former, and but slightly soluble in the latter.

Action of Phosphorus Pentachloride on α -Diphenyl- γ -1-naphthylbutyrolactone.

On heating an equimolecular mixture of the lactone and phosphorus pentachloride on the water-bath, the mass gradually melts to a brownish-red liquid, and a considerable quantity of hydrogen chloride is evolved. Several experiments were made with different preparations which had been recrystallised from various solvents and thoroughly dried, but in no case was the evolution of hydrogen chloride affected; even on employing a cold solution of phosphorus pentachloride in chloroform, a considerable evolution of hydrogen chloride was observed. With the object of isolating the corresponding chloro-ester, a mixture of the lactone (10 grams) with phosphorus pentachloride (8 grams) was heated in the water-bath until the evolution of hydrogen chloride had entirely ceased; the resulting liquid was then poured into about 100 c.c. of absolute alcohol, and heated to boiling for about one hour. The next day the alcoholic liquid was diluted with water, neutralised with sodium carbonate, and extracted with ether. A yellowish-brown, resinous oil was then obtained, which, on cooling, set to a hard, transparent, glassy mass. All attempts to prepare a crystalline product from

this by treatment with solvents were unsuccessful; it was therefore dried at 100° for about ten hours, and then analysed:

0.1969 gave 0.0336 AgCl. $\text{Cl}=4.2$.

$\text{C}_{28}\text{H}_{26}\text{O}_2\text{Cl}$ requires $\text{Cl}=8.3$ per cent.

The product analysed evidently consists of a mixture of a chlorinated substance and an unchlorinated substance in roughly equal amounts. This material did not absorb bromine in the presence of sodium acetate, nor did it decolorise an acetone solution of potassium permanganate even on boiling.

Ethyl $\alpha\gamma$ -Diphenyl- γ -1-naphthylallene- α -carboxylate,
 $\text{C}_{10}\text{H}_7\cdot\text{CPh}\cdot\text{C}\cdot\text{CPh}\cdot\text{CO}_2\text{Et}$.

The impure chloro-ester readily loses hydrochloric acid on boiling with pyridine or quinoline; the reaction, however, takes place much more smoothly with the former, and it is not even necessary to boil the mixture, heating on the water-bath for a few hours being quite sufficient.

In the first experiments, in which the chloro-ester prepared from an equimolecular mixture of lactone and phosphorus pentachloride was employed, many fractional crystallisations were required before pure unsaturated ester was obtained, and the yield was poor.

Better results were obtained as the proportion of phosphorus pentachloride to lactone in the preparation of the chloro-ester was increased, and after a number of experiments had been made, in which these substances were employed in varying proportions, the following method was finally adopted. The chloro-ester is prepared by heating the lactone (1 mol.) with phosphorus pentachloride (2 mols.), and the product of subsequent decomposition with alcohol is heated with twelve times its weight of pyridine for three hours on the water-bath, and then to boiling for a few minutes. After cooling, the liquid is mixed with about twice its volume of ether, and extracted with hydrochloric acid until the pyridine is completely removed. The ethereal liquid is then dried and distilled, and the residue crystallised from boiling alcohol.

The yield amounts to about one-half of the weight of lactone employed. The substance was purified by recrystallisation from glacial acetic acid and alcohol:

0.1964 gave 0.1000 H_2O and 0.6191 CO_2 . $\text{C}=85.97$; $\text{H}=5.65$.

$\text{C}_{28}\text{H}_{24}\text{O}_2$ requires $\text{C}=85.71$; $\text{H}=6.11$ per cent.

$\text{C}_{28}\text{H}_{22}\text{O}_2$ „ $\text{C}=86.15$; $\text{H}=5.64$ „

The substance is readily soluble in hot alcohol, from which it separates almost completely on cooling in stellar aggregates of colourless needles, which turn yellow on heating, and melt at

118.5°. It is readily soluble in acetone, glacial acetic acid, benzene, chloroform, or carbon tetrachloride, and sparingly so in methyl alcohol or light petroleum. A solution of the substance in glacial acetic acid quickly discharges the colour of bromine even in the presence of sodium acetate.

α,γ-Diphenyl-γ-1-naphthylallene-α-carboxylic Acid,
 $C_{10}H_7 \cdot CPh \cdot C : CPh \cdot CO_2H$.

The ester (23 grams) was heated on the water-bath with a mixture of 100 c.c. of *N*-sodium hydroxide and 100 c.c. of pyridine during five hours. The liquid was then diluted considerably with water, boiled until the pyridine was completely removed, cooled, and decomposed with dilute acetic acid. The new acid, which separates as a very voluminous, gelatinous, white precipitate, was collected, washed, and dried on porous porcelain. The substance was then treated with a small quantity of ether, in which it readily dissolves, but separates again almost instantly in the form of a dense, crystalline mass; at the same time a considerable quantity of water separates, and this always adheres to the amorphous acid, even after drying on porous porcelain for several days. The substance can be purified by crystallisation from boiling ether, when it is obtained, on cooling, in the form of large, colourless, transparent, highly refractive, rhombic crystals, which contain ether of crystallisation. For the purification of quantities exceeding one gram, it is expedient to carry out the extraction in a Soxhlet apparatus, owing to the very slight solubility of the substance in ether.

For the determination of the ether of crystallisation, a weighed quantity was heated in a vacuum in a tube immersed in boiling xylene until the weight remained constant:

0.5643 lost 0.0952. $C_4H_{10}O = 16.87$.

0.4840 required 11.2 c.c. *N*/10-sodium hydroxide for neutralisation. Equivalent = 432.

$C_{26}H_{18}O_2, C_4H_{10}O$ requires $C_4H_{10}O = 16.97$ per cent.

Equivalent = 436.

In the preparation of the ether free acid for analysis, a portion of the ether-containing crystals was dissolved in ammonia, the solution heated to expel the ether, cooled, and acidified with hydrochloric acid. The precipitated acid was collected and dried at 100°, and finally purified by crystallisation from benzene:

0.2387 gave 0.7545 CO_2 and 0.1117 H_2O . $C = 86.2$; $H = 5.2$.

0.2474 „ 0.7809 CO_2 „ 0.1103 H_2O . $C = 86.1$; $H = 4.95$.

$C_{26}H_{18}O_2$ requires $C = 86.19$; $H = 4.97$ per cent.

The pure acid can also be readily obtained by crystallising the ether-containing acid from boiling anisole. A portion prepared in this manner was titrated:

0.4830 required 13.4 c.c. *N*/10-sodium hydroxide. Equivalent = 360.

$C_{26}H_{18}O_2$ requires Equivalent = 362.

The acid is slightly soluble in boiling ether, but much less so in cold ether. The ether-containing crystals melt only partly when heated rapidly, the ether evaporating, and the substance then solidifying; on further heating, the substance changes colour at about 180° , and melts indefinitely at $185\text{--}193^\circ$. The acid is readily soluble in acetone or glacial acetic acid, and fairly soluble in benzene, chloroform, or alcohol. It is insoluble in water, but dissolves in dilute aqueous alkalis. On adding sodium hydroxide to a solution of the sodium salt, a white, gelatinous precipitate separates even from very dilute solutions. The acid decolorises a solution of bromine in glacial acetic acid, and an aqueous solution of the sodium salt reacts at once with cold potassium permanganate.

Attempts to Resolve the Acid.

A number of attempts were made to prepare crystalline salts of the acid with the following active bases: quinine, strychnine, brucine, narcotine, cinchonine, cocaine, coniine, aminocamphor, nicotine, and menthylamine. Mixtures of acid and base in suitable organic solvents, such as ether, alcohol, acetone, and chloroform, under varying conditions, in no case gave any crystalline salts. In many instances crystals were deposited, but these were invariably found to consist either of the unchanged acid or base. An attempt was also made to resolve the acid by treating an alcoholic solution with one-half an equivalent of sodium ethoxide and one-half an equivalent of coniine, and fractionally precipitating the coniine salt by successive additions of water. The acids isolated from the various fractions were all found to be inactive.

An attempt was also made to prepare the menthyl ester by heating the acid with menthol, and also the coniide by heating the ester with coniine, but, although interaction occurred, no trace of any crystalline material could be isolated from the neutral gummy products.

Formation of the Unsaturated Bromolactone, $C_{26}H_{17}O_2Br$.

An acetic acid solution of the ester rapidly absorbs bromine, even in the presence of sodium acetate. Titration of the ester with a standardised solution of bromine in glacial acetic acid, employing

potassium iodide as external indicator, proved that one molecule of ester reacts with two atoms of bromine. For the preparation of the bromine compound, a solution of the ester (2 grams) in glacial acetic acid (40 c.c.) was mixed with sodium acetate (1 gram), and then with a 10 per cent. solution of bromine in glacial acetic acid (8.16 c.c.). After some minutes, water was added, when the bromine compound separated as a white, crystalline precipitate. This was collected, washed, and dried, then twice crystallised from boiling glacial acetic acid, washed with alcohol, and dried at 100°:

0.2977 gave 0.7688 CO_2 and 0.1029 H_2O . C=70.43; H=3.84.

0.3105 „ 0.8041 CO_2 „ 0.1086 H_2O . C=70.62; H=3.88.

0.3340 „ 0.8660 CO_2 „ 0.1159 H_2O . C=70.70; H=3.80.

0.2526 „ 0.1064 AgBr. Br=17.92.

$\text{C}_{26}\text{H}_{17}\text{O}_2\text{Br}$ (unsaturated bromolactone) requires C=70.75;
H=3.85; Br=18.14 per cent.*

The substance is fairly soluble in boiling glacial acetic acid, from which it separates on cooling in slender, colourless needles, which melt on heating at 192°. It is only very sparingly soluble in alcohol, ether, or benzene, almost insoluble in light petroleum, but fairly readily soluble in boiling acetone or chloroform. It does not decolorise a solution of bromine in glacial acetic acid or a solution of potassium permanganate in acetone.

Action of Mineral Acids on the Unsaturated Carboxylic Acid.

On heating a solution of diphenylnaphthylallenecarboxylic acid in glacial acetic acid, to which a few drops of concentrated hydrochloric acid have been added, a white, crystalline powder separates. The mixture was heated on the water-bath until no further separation took place (about one hour), the crystalline precipitate was then collected, and crystallised from boiling glacial acetic acid:

0.2375 gave 0.7474 CO_2 and 0.1094 H_2O . C=85.83; H=5.11.

$\text{C}_{26}\text{H}_{18}\text{O}_2$ requires C=86.16; H=4.97 per cent.

The substance is readily soluble in acetone, glacial acetic acid, benzene, chloroform, or ethyl acetate, sparingly so in boiling alcohol, but almost insoluble in the cold. It does not decolorise an acetone solution of potassium permanganate even on boiling. It does not dissolve appreciably in boiling aqueous sodium carbonate or sodium hydroxide, and is only very slowly attacked by boiling ethyl- or amyl-alcoholic sodium hydroxide. It is reduced on adding sodium or sodium amalgam to the hot amyl-alcoholic solution. In both cases, however, all attempts to isolate a

* $\text{C}_{28}\text{H}_{23}\text{O}_2\text{Br}$ (bromo-ester) requires C=71.34; H=4.88. Br=16.98.

$\text{C}_{26}\text{H}_{19}\text{O}_2\text{Br}$ (bromo-lactone) „ C=70.41; H=4.32. Br=18.05.

crystalline substance from the reduction product were unsuccessful, and no indication could be obtained of the formation of the saturated lactone or of the hydroxy-acid corresponding with it.

Some of the expense of this work was defrayed by the aid of a Government grant from the Royal Society, for which the authors desire to express their thanks.

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VI.—*The Production of para-Diazoimides from Alkyl- and Aryl-sulphonyl-para-diamines. A General Reaction.*

By GILBERT T. MORGAN and JOSEPH A. PICKARD, B.Sc., A.R.C.S.

CERTAIN derivatives of *p*-phenylenediamine give rise to diazonium salts, from which diazoimines or diazoimides may be produced by internal condensation. The earliest known *p*-diazoimine is the explosive phenyl-*p*-diazoiminobenzene, $\text{C}_6\text{H}_5\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2$, discovered

by Ikuta (*Annalen*, 1888, **243**, 282), and afterwards studied by Hantzsch (*Ber.*, 1902, **35**, 895). In 1904, one of us, in conjunction with F. M. G. Mickelthwait, obtained the first *p*-diazoimide from camphor- β -sulphonyl-*p*-phenylenediamine (*Trans.*, 1905, **87**, 74), and subsequently showed that benzenesulphonyl-*p*-phenylenediamine and its homologues readily yield arylsulphonyl-*p*-phenylenediazoimides (*Trans.*, 1905, **87**, 921, 1302).

Although these diazoimides are moderately stable substances, yet comparative experiments proved that they and Ikuta's unstable diazoimine are members of the same class of diazo-compounds. This relationship was demonstrated by the preparation of a connecting series of mono-, di-, and tri-nitrophenyl-*p*-phenylenediazoimines, the stability of which increases as nitro-groups are introduced successively into the molecule of *p*-aminodiphenylamine (*Trans.*, 1908, **93**, 605).

These *p*-diazoimines and *p*-diazoimides are distinguished from the *o*-diazoimines and *o*-diazoimides by their intense colour, generally either yellow or orange, and by their very reactive character. When treated with cold concentrated mineral acids, they regenerate the corresponding diazonium salts, and with phenols and aromatic amines they couple additively to form azo-derivatives. On account of these properties, some of the more readily prepared

members of the group can be turned to account in the production of azo-colouring matters (*J. Soc. Dyers*, 1909, **25**, 107).

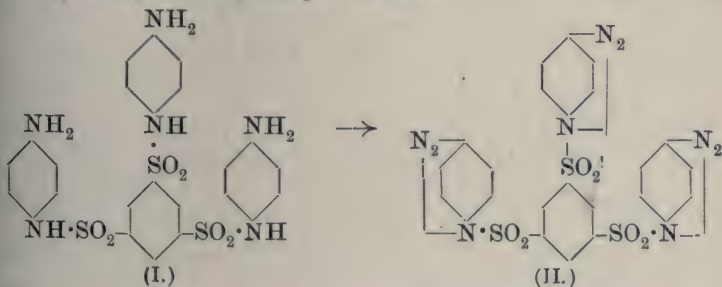
These results render plausible the view that the property of forming *p*-diazotimino-compounds is possessed by all derivatives of *p*-phenylenediamine having the formula $\text{RNH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, and even by the base itself, but more experimental evidence would be required before it could be definitely stated that the reaction is a perfectly general one.

By the experiments described in the present communication we have endeavoured to show that, in all probability, the reaction is general for all organic sulphonyl derivatives of *p*-phenylenediamine. This demonstration may be conveniently divided into three stages.

I.—*Para-diazoimides Containing Arylpolysulphonyl Groups.*

The conversion of benzene-1:3-disulphonylbis-*p*-phenylenediamine into the corresponding bis-diazoimide has already been accomplished (*Trans.*, 1905, **87**, 1309), and, in the present instance, the case of *benzene-1:3:5-trisulphonylter-p-phenylenediamine* (I) has been examined as a typical example of an amide derived from a complex polysulphonic acid.

Apart from certain practical difficulties encountered in the preparation of the triamine, it was found that the conversion of this base into *benzene-1:3:5-trisulphonylter-p-phenylenediazoimide* (II) is a comparatively simple matter:



This result justifies the conclusion that the production of the diazoimide is independent of the number of sulphonyl groups present in the molecule of the aromatic aminosulphonamide.

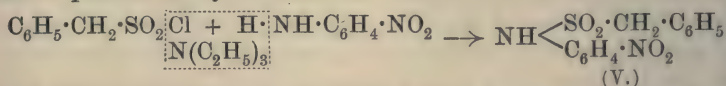
II.—*Para-diazoimides Containing Mixed Aryl-alkylsulphonyl Groups.*

Former experiments on the constitution of diazoimides led to the interesting observation that ω -benzenesulphonyl-*o*-benzylene-

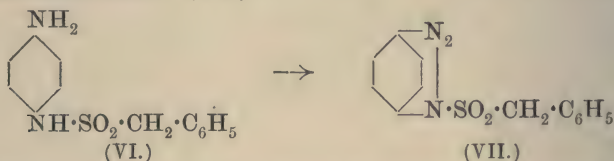
diamine (III) gives rise to a diazoimide (IV) of mixed type (Trans., 1906, **89**, 1162):



but as the substituent groups of this product differ in their orientation from those of the *p*-diazoimides, we now endeavoured to obtain a mixed aryl-alkyl derivative of the general type by starting from *toluene- ω -sulphonyl-*p*-nitroaniline* (V). The preparation of this substance presented some difficulty, however, owing to the circumstance that toluene- ω -sulphonyl chloride, unlike the arylsulphonyl chlorides, does not condense satisfactorily with *p*-nitroaniline in pyridine or boiling toluene. The addition of triethylamine to the latter solvent was finally found to bring about the desired result, the following condensation then taking place almost quantitatively:



*Toluene- ω -sulphonyl-*p*-phenylenediamine* (VI), prepared by reducing the nitro-compound (V), when successively diazotised and treated with aqueous sodium acetate, furnishes *toluene- ω -sulphonyl-*p*-phenylenediazoimide* (VII):



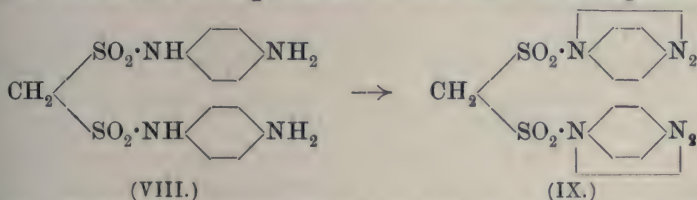
This substance, containing a mixed aromatic-alkyl group, behaves like a typical *p*-diazoimide; it separates in bright yellow, sparingly soluble needles, regenerates the diazonium chloride with cold concentrated hydrochloric acid, and couples with phenols and aromatic amines, yielding azo-derivatives.

III.—*Para-diazoimides Containing Alkylsulphonyl Groups.*

The existence of camphor- β -sulphonyl-*p*-phenylenediazoimide (*loc. cit.*) shows that the presence of an aromatic group attached to the sulphur atom is not an essential condition for the formation of a diazoimide of this type, and accordingly we took steps to obtain diazoimino-derivatives containing the simplest alkylsulphonyl groups.

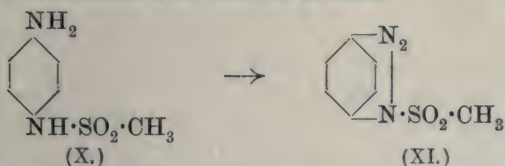
Methionie chloride condenses readily with *p*-nitroaniline, yielding *methanedisulphonylbis-p*-nitroaniline, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$, which, on reduction, gives rise to *methanedisulphonylbis-p*-phenylenediamine (VIII), an amphoteric substance, yielding both a sodium derivative and a dihydrochloride. The latter compound, when diazotised, furnishes a fairly stable *bisdiazonium chloride*, the colourless solution of which turns yellow on the addition of aqueous sodium acetate, thus indicating the formation of a diazoimide.

Methanedisulphonylbis-p-phenylenediazoimide (IX) is, however, isolated only when either the dry diazonium chloride is dusted into concentrated aqueous sodium acetate, or when crystals of this salt are added to a strong solution of the diazonium compound:



This diazoimide has the physical and chemical properties which characterise the group, but is less stable than the more complex members. It is somewhat soluble in water, although the solubility is considerably diminished in the dried specimens.

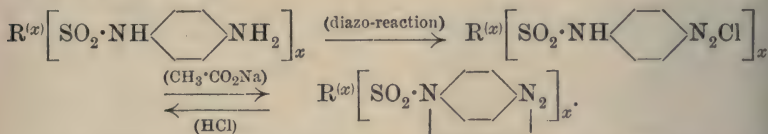
The production of the simplest possible alkylsulphonyl-*p*-phenylenediazoimide has been accomplished by the following series of operations. *Methanesulphonyl-p*-nitroaniline, produced by condensing methanesulphonyl chloride and *p*-nitroaniline in the presence of triethylamine, yields, on reduction, *methanesulphonyl-p*-phenylenediamine (X). The diazonium chloride and sulphate of this base are colourless salts, which give yellow solutions of the diazoimide on treatment with sodium acetate:



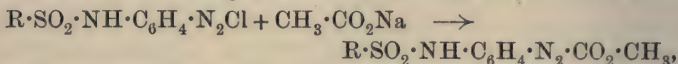
Methanesulphonyl-p-phenylenediazoimide (XI) is soluble in water, and as it rapidly decomposes into a resinous product even in cold aqueous solutions, its isolation in the solid state is a matter of considerable difficulty. When silver nitrite is introduced into a solution of methanesulphonyl-*p*-phenylenediamine hydrochloride, silver chloride is precipitated, and the solution then contains only the diazoimide, which may be obtained by evaporating to dryness

in a vacuum over phosphoric oxide. Unless this evaporation is effected very rapidly, the product darkens, and some loss of nitrogen is apparent. When sodium nitrite is used in this experiment, the filtered solution contains molecular proportions of the diazoimide and sodium chloride. The presence of this inorganic salt seems to increase the stability of the diazoimide, and the solution may be evaporated to dryness in a vacuum without loss of nitrogen.

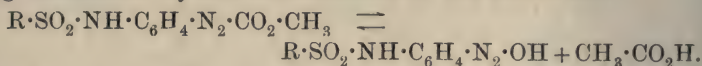
With the production of the two foregoing diazoimides, containing respectively methanesulphonyl and methanedisulphonyl groups, the task of demonstrating the general character of this chemical change is completed, and the reaction may be expressed in general terms in accordance with the following symbolical scheme, where R is any alkyl, aromatic, hydroaromatic, or mixed aromatic-alkyl radicle, and x is its valency:



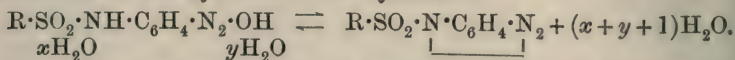
The conversion of the diazonium chloride into the *p*-diazoimide is a reversible change, and it is of interest, in connexion with the modern theories of solution, to notice that the reaction probably occurs in three or more successive phases. The inverse change is brought about, not only by mineral acids, but even by acetic acid when present in excess, and this result indicates that the first phase in the direct change is the formation of a diazonium acetate:



which, in the absence of any considerable excess of free acetic acid, undergoes hydrolysis, the extent to which this second phase occurs being determined by the concentration of the acetic acid:

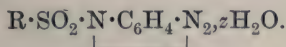


The hypothetical diazo-hydroxide thus produced is an amphoteric substance, having an acidic substituent, $\text{R} \cdot \text{SO}_2 \cdot \text{NH}$, and a basic group, $\text{N}_2 \cdot \text{OH}$, each of which probably exists in solution in association with a certain characteristic number of water molecules. But as the sodium acetate solution invariably assumes the yellow colour of the *p*-diazoimide, one must suppose that a certain proportion of this substance is actually formed in solution by the internal condensation of the hydrated diazo-hydroxide:



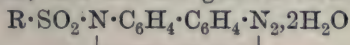
This mode of representing the final phase of the condensation is

probably true only when R is a complex group of comparatively high molecular weight. In these cases, the precipitation of the *p*-diazoidimide is immediate and practically complete, but when R is a simple alkyl group of low molecular weight, the *p*-diazoidimide exhibits a tendency to remain in solution, probably in the hydrated form:



Methanesulphonyl-*p*-phenylenediazoidimide is obtained only on evaporating its solution to dryness under greatly reduced pressure, and methanedisulphonylbis-*p*-phenylenediazoidimide in the moist condition dissolves fairly readily in cold water, and becomes much less soluble only after desiccation over phosphoric oxide.

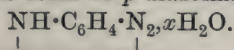
Further evidence for the existence of hydrated forms of the diazoidimides was obtained by F. M. G. Micklethwait, J. M. Hird, and one of us in the study of the arylsulphonylbenzidines. In these bases, where the acid and basic substituents are separated by two aromatic nuclei, the diazoidimide separates with two molecular proportions of water, and has the general formula:



(Trans., 1907, **91**, 1509; 1908, **93**, 615).

The closely allied aromatic diazo-oxides exhibit the same phenomenon; the more complex members of the series separate in anhydrous forms, as, for example, dinitrophenylenediazo-oxide, $\text{O} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_2 \cdot \text{N}_2$, whereas Hantzsch and Davidson (*Ber.*, 1896, **29**, 1530) found that the simplest member, *p*-phenylenediazo-oxide, separates with four molecules of water, and can be represented by the formula $\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{N}_2, 4\text{H}_2\text{O}$.

In connexion with the existence of hydrated forms of diazoimines, attention should be directed to an interesting observation made by the chemists of the Badische Anilin- und Soda-Fabrik (D.R.-P. 205037). Acetyl-*p*-phenylenediamine was diazotised in hydrochloric acid, and the acetyldiazonium chloride hydrolysed by gently heating the solution. The dissolved product was then found to couple with alkaline β -naphthol much less rapidly than the unhydrolysed acetyl-*p*-aminobenzenediazonium chloride. Although the product of hydrolysis was not isolated, it seems probable that it consists of a hydrated form of *p*-diazoinimobenzene,



EXPERIMENTAL.

I.—*Benzene-1: 3: 5-trisulphonylter-p-phenylenediazoimide.*

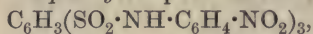
A mixture of benzene-1: 3: 5-trisulphonyl chloride (1 mol.) and *p*-nitroaniline (3 mols.) was boiled in dry pyridine for several hours, the solvent then removed by evaporation, and the residue, after extraction with water, was boiled with aqueous sodium carbonate. The alkaline filtrate, when acidified with dilute hydrochloric acid, yielded a yellowish-white precipitate, which, after repeated crystallisation from methyl alcohol, separated as a white, crystalline powder, and melted at 278° :

0.2202 gave 23.6 c.c. N_2 at 17° and 758.2 mm. $N=12.58$.

0.2100 „ 0.2162 $BaSO_4$. $S=14.15$.

$C_{24}H_{18}O_{12}N_6S_3$ requires $N=12.40$; $S=14.19$ per cent.

Benzene-1: 3: 5-trisulphonylter-p-nitroaniline,



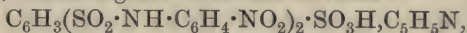
is a distinctly acidic substance, and on treatment with alcoholic potash gives a potassium derivative, separating in small, yellow crystals.

When diluted with an equal volume of water, the methyl-alcoholic mother liquors of the preceding compound deposited a brown oil, which gradually solidified to radiating clusters of stout, yellow prisms. This product, when washed with cold ethyl acetate and crystallised from alcohol, was obtained in odourless, yellow crystals, insoluble in water or dilute hydrochloric acid, but dissolving in cold aqueous sodium hydroxide to a yellow solution having a strong odour of pyridine:

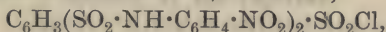
0.1288 gave 12.8 c.c. N_2 at 24° and 763 mm. $N=11.19$.

$C_{23}H_{19}O_{11}N_5S_3$ requires $N=11.01$ per cent.

This result, which agrees with the formula:



shows that a certain amount of the chloride,



arises from the interaction of *p*-nitroaniline and benzene-1: 3: 5-trisulphonyl chloride, the subsequent action of water in the presence of pyridine leading to the production of the above pyridine salt.

A comparative experiment made with the other nitroanilines showed that the ortho-base gave only a small yield of crystalline product with benzene-1: 3: 5-trisulphonyl chloride, whereas the meta-base reacted readily and quantitatively in boiling pyridine to form the following compound.

Benzene-1: 3: 5-trisulphonylter-m-nitroaniline,



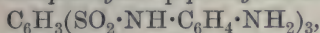
separated from pyridine by removing the latter with cold dilute hydrochloric acid, was crystallised from 50 per cent. acetic acid, and thus obtained in small, white needles, melting at 199° :

0.2657 gave 27.4 c.c. N_2 at 14° and 767.4 mm. $N=12.28$.

$C_{24}H_{18}O_{12}N_6S_3$ requires $N=12.40$ per cent.

This trisulphonamide is readily soluble in aqueous alkali hydroxides or glacial acetic acid.

Benzene-1: 3: 5-trisulphonylter-p-phenylenediamine,



was produced by adding iron filings (10 grams) to benzene-1: 3: 5-trisulphonylter-p-nitroaniline suspended in 100 c.c. of warm water containing 1 c.c. of glacial acetic acid, the mixture being heated for three hours. Excess of sodium bicarbonate was added, the mixture filtered, and the filtrate acidified with acetic acid, when the triamine separated, the yield being about 50 per cent. When crystallised from water or acetone, the triamine separated in colourless nodules, and melted at 256° :

0.1580 gave 19.5 c.c. N_2 at 23° and 775 mm. $N=14.55$.

$C_{24}H_{24}O_4N_4S_3$ requires $N=14.29$ per cent.

The diazo-solution from 1 gram of base, 30 c.c. of 2*N*-hydrochloric acid, and 20 per cent. sodium nitrite solution was treated with aqueous sodium acetate until a slight permanent precipitate was formed. From the filtered solution, excess of sodium acetate deposited the diazoimide as a light yellow, microcrystalline precipitate, which was washed successively with cold water, alcohol, and ether. The product retained water very tenaciously, its weight becoming constant only after prolonged drying over sulphuric acid or phosphoric oxide:

0.1923 gave 0.3244 CO_2 and 0.0502 H_2O . $C=45.99$; $H=2.70$.

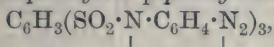
0.1988 „ 34.8 c.c. N_2 at 18° and 757.3 mm. $N=19.75$.

0.2011 „ 0.2235 $BaSO_4$. $S=15.26$.

$C_{24}H_{15}O_6N_9S_3$ requires $C=46.37$; $H=2.43$; $N=20.32$;
 $S=15.46$ per cent.

The filtrate from the diazoimide gave a red coloration with alkaline β -naphthol, showing that the precipitation of the condensation product was not complete even in the presence of considerable excess of sodium acetate.

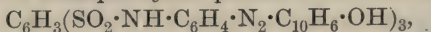
Benzene-1: 3: 5-trisulphonylter-p-phenylenediazoimide,



which explodes somewhat violently at 146° , is too insoluble to be crystallised from the ordinary organic solvents; it can be preserved for an indefinite time in the dark, although on exposure to light it rapidly darkens and assumes a purple-brown colour. When

dissolved in cold hydrochloric acid, the diazoimide is converted into diazonium chloride, as may be shown by adding the diluted solution to alkaline β -naphthol.

Benzene-1: 3: 5-trisulphonylter-p-aminobenzeneazo- β -naphthol,



obtained either in the preceding reaction or by triturating the diazoimide with β -naphthol in the presence of pyridine, separated from alcohol as a dark red, crystalline powder, melting at 265—266°:

0.1060 gave 10.4 c.c. N_2 at 21.5° and 762 mm. $\text{N}=11.39$.

$\text{C}_{54}\text{H}_{48}\text{O}_9\text{N}_9\text{S}_3$ requires $\text{N}=11.92$ per cent.

This azo- β -naphthol dissolves in concentrated sulphuric acid to a deep red solution; its alkali salts are sparingly soluble in water containing alkali hydroxides, and are decomposed by dilute acetic acid.

II.—*Toluene- ω -sulphonyl-p-phenylenediazoimide.*

It was not found possible to condense *p*-nitroaniline and toluene- ω -sulphonyl chloride in boiling toluene, and in warm pyridine these substances interacted to form tarry products. The difficulty was overcome by dissolving molecular proportions of *p*-nitroaniline, toluene- ω -sulphonyl chloride, and triethylamine in toluene, the liquids being first carefully dried over sodium. After boiling for two to three hours, the condensation was complete, and the solvent was then removed by evaporation. The residue was extracted repeatedly with boiling aqueous sodium carbonate, and the solution filtered while hot. On cooling, the sparingly soluble orange sodium derivative, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{NNa}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, separated; this was decomposed at 0° with dilute hydrochloric acid, when the *toluene- ω -sulphonyl-p-nitroaniline*, which first appeared as a pasty, yellow mass, slowly solidified, and was crystallised from alcohol and water (1: 4):

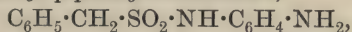
0.1452 gave 12.5 c.c. N_2 at 15° and 737 mm. $\text{N}=9.82$.

0.1075 „ 0.0868 BaSO_4 . $\text{S}=11.09$.

$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_2\text{S}$ requires $\text{N}=9.60$ and $\text{S}=10.96$ per cent.

After repeated crystallisation from dilute alcohol, the sulphonamide melts at 155°.

Toluene- ω -sulphonyl-p-phenylenediamine,



was produced in almost quantitative yield by reducing the preceding nitro-compound (4 grams) with iron filings (5 grams) in 100 c.c. of 4 per cent. acetic acid. After boiling for thirty minutes, the mixture, rendered alkaline with sodium carbonate, was filtered, when the filtrate deposited white crystals of the base, a further quantity being extracted from the residue with alcohol. After

crystallisation from this solvent, the base was obtained in acicular prisms, melting at 121—122°:

0.1241 gave 11.8 c.c. N_2 at 16° and 753.5 mm. $N=11.20$.

$C_{13}H_{14}O_2N_2S$ requires $N=10.69$ per cent.

This diamine was diazotised in 6 per cent. hydrochloric acid, and the filtered solution treated with excess of aqueous sodium acetate. The liquid became yellow, and subsequently deposited lemon-yellow needles of the diazoimide. These were washed successively with cold water, alcohol, and ether. The aqueous filtrate gave only a slight coloration with β -naphthol, showing that the precipitation of diazoimide was complete. The product, a typical diazoimide, darkened at 136°, and decomposed violently at 141°:

0.1463 gave 0.3061 CO_2 and 0.0567 H_2O . $C=57.05$; $H=4.31$.

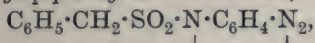
0.1136 „ 15.9 c.c. N_2 at 18° and 735 mm. $N=15.63$.

0.1279 „ 0.1056 $BaSO_4$. $S=11.33$.

$C_{13}H_{11}O_2N_3S$ requires $C=57.14$; $H=4.03$; $N=15.38$;

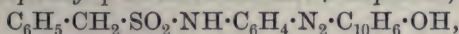
$S=11.73$ per cent.

Toluene- ω -sulphonyl-p-phenylenediazoimide,



like the arylsulphonyldiazoimides, is practically insoluble in the ordinary solvents, but dissolves in cold hydrochloric acid, regenerating the diazonium chloride. Although stable in the dark, it rapidly darkens on exposure to light, becoming orange, and finally dark brown.

Toluene- ω -sulphonyl-p-aminobenzeneazo- β -naphthol,



prepared either by triturating the diazoimide with β -naphthol and pyridine, or by adding the acid solution of the diazoimide to alkaline β -naphthol, separated from alcohol as a bright red, crystalline powder, melting at 211°:

0.2110 gave 19 c.c. N_2 at 12° and 763 mm. $N=10.68$.

$C_{23}H_{19}O_3N_3S$ requires $N=10.10$ per cent.

[With F. M. G. MICKLETHWAIT.]

III.—*Methanedisulphonylbis-p-phenylenediazoimide.*

When methionie chloride* (1 mol.) and *p*-nitroaniline (2 mols.) were mixed in dry toluene, a vigorous reaction took place, and the condensation was completed by warming the mixture for a few minutes. After removing the toluene by evaporation, the residue

* For the specimen of methionie chloride employed in the following experiments, we are indebted to the liberality of the Farbenfabriken vormals Friedrich Bayer & Co.

was extracted successively with boiling water to remove *p*-nitroaniline, and with aqueous sodium carbonate to dissolve the *methanedisulphonylbis-p*-nitroaniline, $\text{CH}_2(\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2)_2$. The latter substance was then crystallised from alcohol, when it separated in transparent, light yellow prisms, melting and decomposing at 248—249°:

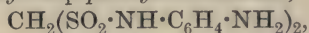
0.1607 gave 19.0 c.c. N_2 at 25° and 774 mm. $\text{N}=13.54$.

0.1871 „ 0.2216 BaSO_4 . $\text{S}=16.27$.

$\text{C}_{13}\text{H}_{12}\text{O}_8\text{N}_4\text{S}_2$ requires $\text{N}=13.48$; $\text{S}=15.41$ per cent.

Methanedisulphonylbis-p-nitroaniline decomposes both soluble and insoluble carbonates; its sodium derivative is somewhat sparingly soluble in cold water.

Methanedisulphonylbis-p-phenylenediamine,



was prepared by reducing the preceding compound with iron filings and 4 per cent. acetic acid. The reduction was completed after two hours' heating, and the mixture, rendered alkaline with sodium carbonate, was rapidly filtered. The base, which had passed into the filtrate in the form of its sodium derivative, was precipitated with dilute acetic acid, and crystallised from ethyl acetate, when it separated in small, colourless needles, melting at 227°:

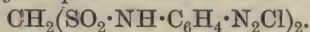
0.1505 gave 21.0 c.c. N_2 at 26° and 771 mm. $\text{N}=15.72$.

0.2036 „ 0.2691 BaSO_4 . $\text{S}=18.15$.

$\text{C}_{13}\text{H}_{16}\text{O}_4\text{N}_4\text{S}_2$ requires $\text{N}=15.73$; $\text{S}=17.97$ per cent.

Methanedisulphonylbis-p-phenylenediamine is an amphoteric substance, exhibiting in a remarkable degree the dual properties of base and acid. As a base, it forms a dihydrochloride soluble in water, and dissolving more sparingly in alcohol. As an acid, it decomposes calcium carbonate and other insoluble carbonates, and forms soluble sodium and even ammonium derivatives.

Methanedisulphonylbis-p-aminobenzenediazonium chloride,



—The foregoing base was suspended in alcohol, concentrated hydrochloric acid added, and the resulting solution rapidly filtered. Amyl nitrite was then added, when the diazonium chloride rapidly separated as a light grey, crystalline precipitate, insoluble in alcohol:

0.1114 gave 17.6 c.c. N_2 at 22° and 769 mm. $\text{N}=18.10$.

0.2090 „ 0.1276 AgCl . $\text{Cl}=15.10$.

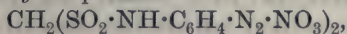
$\text{C}_{13}\text{H}_{12}\text{O}_4\text{N}_6\text{Cl}_2\text{S}_2$ requires $\text{N}=18.60$; $\text{Cl}=15.74$ per cent.

When prepared in the dark, the diazonium chloride is almost colourless, but when exposed to light in contact with its mother

liquor, the salt frequently assumes a reddish-brown colour, and becomes almost insoluble in water.

The corresponding diazonium sulphate was produced by diazotising the foregoing diamine in dilute sulphuric acid, and, being less soluble than the diazonium chloride, it was precipitated by alcohol from its aqueous solution. These salts, when dissolved in water, have an acid reaction.

Methanedisulphonylbis-p-aminobenzenediazonium nitrate,



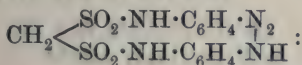
and the following substance were obtained in unsuccessful attempts to prepare the bisdiazoidime. The nitrate was formed by adding silver nitrate to an aqueous solution of the foregoing diazonium chloride, and concentrating the filtrate from the silver chloride over potassium hydroxide under 5 mm. pressure. It separated in pale yellow needles, which, when dry, were somewhat sparingly soluble in cold water, and decomposed violently at 156–160°:

0.0898 gave 17.7 c.c. N_2 at 22° and 766 mm. $\text{N}=22.51$.

0.1368 „ 0.1580 CO_2 and 0.0365 H_2O . $\text{C}=31.50$; $\text{H}=2.96$.

$\text{C}_{13}\text{H}_{12}\text{O}_{10}\text{N}_8\text{S}_2$ requires $\text{C}=30.95$; $\text{H}=2.38$; $\text{N}=22.22$ per cent.

A carefully purified portion of methanedisulphonylbis-p-phenylenediamine was dissolved in glacial acetic acid, and diazotised with ethyl nitrite. The filtered solution, when gradually diluted with alcohol and ether, deposited a pale yellow, unstable substance, which, when rapidly collected and dried, gave analytical data corresponding with the diazoamine:



0.1134 gave 0.1722 CO_2 and 0.0452 H_2O . $\text{C}=41.41$; $\text{H}=4.43$.

0.1324 „ 22.0 c.c. N_2 at 17° and 772 mm. $\text{N}=19.60$.

$\text{C}_{13}\text{H}_{13}\text{O}_4\text{N}_5\text{S}_2$ requires $\text{C}=42.50$; $\text{H}=3.54$; $\text{N}=19.07$ per cent.

Another portion of the base was dissolved in glacial acetic acid, diazotised with ethyl nitrite, and the solution evaporated to dryness at the ordinary temperature in a vacuum desiccator. The residue, a dark red substance resembling shellac, contained no combined acetic acid, and only 15.38 per cent. of nitrogen, showing that a portion of the diazo-nitrogen had been eliminated during evaporation. Its composition approximated to that of a diazo-oxide or azo-phenol produced by internal condensation.

The colourless aqueous solutions of the bisdiazonium salts, when treated with excess of sodium acetate, assumed an intense yellow colour, indicating the formation of the bisdiazoidime, but the substance was not precipitated. After many fruitless attempts to isolate the bisdiazoidime, it was found possible to precipitate it

either by adding the solid bisdiazonium chloride to concentrated aqueous sodium acetate or by introducing crystals of the latter salt into strong aqueous solutions of the bisdiazonium chloride. The latter procedure is preferable, because by the former the product passes through a viscid phase which is obviated by the second method of mixing. The bisdiazoidime separates as an orange-yellow, microcrystalline mass, which, when once segregated, is remarkably insoluble in cold water, and can accordingly be thoroughly washed without serious loss, first with water, and then successively with ether and light petroleum:

0.1042 gave 0.1576 CO_2 and 0.0368 H_2O . $\text{C}=41.26$; $\text{H}=3.87$.

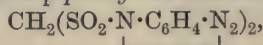
0.1272 „ 0.1926 CO_2 „ 0.0414 H_2O . $\text{C}=41.29$; $\text{H}=3.61$.

0.1123 „ 21.9 c.c. N_2 at 19.5° and 761 mm. $\text{N}=22.43$.

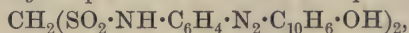
0.1712 „ 0.2138 BaSO_4 . $\text{S}=17.15$.

$\text{C}_{13}\text{H}_{10}\text{O}_4\text{N}_6\text{S}_2$ requires $\text{C}=41.26$; $\text{H}=2.64$; $\text{N}=22.22$;
 $\text{S}=16.93$ per cent.

Methanedisulphonylbis-p-phenylenediazoimide,



decomposes violently at 120° , and darkens rapidly on exposure to light. When triturated with β -naphthol in the presence of pyridine, it combined additively with the former, giving rise to *methanedisulphonylbis-p-aminobenzeneazo- β -naphthol*,



which was also produced in the form of its sparingly soluble dark red alkali derivative on adding the bisdiazonium chloride to alkaline β -naphthol. The free azo- β -naphthol is a red powder, varying considerably in tint, and only sparingly soluble in the ordinary organic media; it melts at 272° :

0.1304 gave 14.4 c.c. N_2 at 15° and 752 mm. $\text{N}=12.80$.

$\text{C}_{13}\text{H}_{26}\text{O}_6\text{N}_6\text{S}_2$ requires $\text{N}=12.61$ per cent.

IV.—*Methanesulphonyl-p-phenylenediazoimide*.

The methanesulphonyl chloride employed in the following experiments was either purchased or prepared from methyl sulphate, this ester being converted into methyl thiocyanate by means of aqueous potassium thiocyanate. Methanesulphonic acid was then produced by oxidising methyl thiocyanate with nitric acid, and freed from water as completely as possible by repeated evaporation. Treatment with phosphorus pentachloride led to the formation of a mixture of phosphoryl chloride and methanesulphonyl chloride, which was fractionated under the ordinary and also under reduced pressure. All the specimens of methanesulphonyl chloride employed contained appreciable amounts of phosphorus compounds, which,

fortunately, did not interfere seriously with the following condensation.

Methanesulphonyl-p-nitroaniline, $\text{CH}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$.

Ten grams of methanesulphonyl chloride were added to a warm toluene solution of *p*-nitroaniline (10.5 grams) and triethylamine (10 grams); a heavy, oily layer separated, and rings of triethylamine hydrochloride were projected from the flask. After boiling for fifteen minutes, the solvent was evaporated off, and the residue extracted with excess of aqueous sodium carbonate until only a slight amount of tar remained undissolved. The solution was thoroughly cooled, and the crystallised *p*-nitroaniline separated; the filtrate acidified with hydrochloric acid gave an almost colourless precipitate of methanesulphonyl-*p*-nitroaniline, the yield being about 9 to 10 grams.

Very little condensation occurs in the absence of triethylamine, and in this respect methanesulphonyl chloride differs considerably from methionic chloride, which reacts energetically with *p*-nitroaniline, even in the absence of any condensing agent.

Methanesulphonyl-*p*-nitroaniline crystallises readily from dilute alcohol in pale yellow needles or transparent, amber-coloured prisms; it melts at 186° :

0.1212 gave 13.9 c.c. N_2 at 20° and 756 mm. $\text{N} = 13.06$.

$\text{C}_7\text{H}_8\text{O}_4\text{N}_2\text{S}$ requires $\text{N} = 12.96$ per cent.

This nitro-compound dissolves readily in aqueous sodium carbonate or ammonia, and is slightly soluble in water; it is not reprecipitated from its alkaline solutions by acetic acid, but only by mineral acids.

Methanesulphonyl-p-phenylenediamine, $\text{CH}_3\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$.

The foregoing nitro-compound could not be reduced satisfactorily by iron and dilute acetic acid, zinc and ammonia, aluminium amalgam, stannous chloride, or ammonium sulphide. The best result was obtained by dissolving 2 grams of nitro-compound in 20 c.c. of 50 per cent. alcohol, containing 0.5 gram of ammonium chloride. On adding excess of zinc dust to the warm solution, reduction occurred, and was completed by boiling for a short time. The alcoholic filtrate was rapidly evaporated to dryness, and the residue extracted with benzene. When crystallised from this solvent, the base separated in colourless needles, melting at 122° :

0.1327 gave 18.1 c.c. N_2 at 20° and 772 mm. $\text{N} = 15.86$.

0.1588 „ 0.2036 BaSO_4 . $\text{S} = 17.60$.

$\text{C}_7\text{H}_{10}\text{O}_2\text{N}_2\text{S}$ requires $\text{N} = 15.05$; $\text{S} = 17.20$ per cent.

The *hydrochloride* of methanesulphonyl-*p*-phenylenediamine, which is readily soluble in water or alcohol, separates in colourless leaflets, melting at 223° :

0.1192 gave 12.7 c.c. N_2 at 21.5° and 761 mm. $N=12.11$.

$C_7H_{10}O_2N_2S.HCl$ requires $N=12.53$ per cent.

The sulphate is somewhat less soluble in water, and is precipitated by alcohol from its aqueous solution. The diazonium chloride separated in colourless plates on adding successively ethyl nitrite and dry ether to an alcoholic solution of the hydrochloride; it rapidly becomes brown and viscid on exposure to the atmosphere. The diazonium sulphate was more stable than the diazonium chloride, and separated in colourless crystals on adding ethyl nitrite and ether successively to a solution of the sulphate in glacial acetic acid.

These diazonium salts, when added to strong aqueous solutions of sodium acetate, gave either a resinous product or an intensely yellow solution, the result depending on the concentration of the sodium acetate. Only in two isolated cases was a yellow, crystalline product obtained in this way. This compound decomposed violently on gently warming, whereas the resinous product burnt quietly. The former of these substances was evidently the diazoimide, as was proved by coupling it with β -naphthol.

The diazoimide was obtained in the solid condition by mixing cold aqueous solutions of methanesulphonyl-*p*-phenylenediamine hydrochloride and sodium nitrite, taking these salts in accurately weighed molecular proportions. The solution was rapidly filtered four or five times, and when of a clear yellow colour was evaporated at the ordinary temperature in a vacuum desiccator over phosphoric oxide and potassium hydroxide. An orange-yellow residue was obtained, consisting of the diazoimide (decomposition point 150°) and sodium chloride in approximately molecular proportions. The mixture was ground up thoroughly, and the sodium chloride estimated as sodium sulphate after heating with pure concentrated sulphuric acid. After making allowance for the proportion of sodium chloride present, the following results were obtained:

0.1765 gave 0.2668 CO_2 and 0.0646 H_2O . $C=41.23$; $H=4.06$.

0.1353 „, 25.5 c.c. N_2 at 20° and 772 mm. $N=21.90$.

$C_7H_7O_2N_3S$ requires $C=42.64$; $H=3.65$; $N=21.31$ per cent.

The diazotisation was now repeated, using silver nitrite instead of sodium nitrite, the dry salt being thoroughly triturated with the aqueous solution of methanesulphonyl-*p*-phenylenediamine hydrochloride. After filtering off the silver chloride, the clear yellow solution contained only the methanesulphonyl-*p*-phenylene-diazoimide; the substance appeared, however, to be less stable than

in the presence of sodium chloride, and showed signs of losing some of its diazo-nitrogen. The final residue was shown to contain diazoimide by coupling with β -naphthol in pyridine solution. A bright red azo- β -naphthol was produced, which melted at $244\text{--}245^\circ$, and was identical with *methanesulphonyl-p-aminobenzeneazo- β -naphthol*, prepared by coupling methanesulphonyl-*p*-aminobenzene-diazonium chloride with alkaline β -naphthol. In the latter preparation the azo- β -naphthol was produced in the form of its soluble alkali derivative, and was precipitated by dilute acetic acid. The free azo- β -naphthol was almost insoluble in alcohol, but crystallised readily from glacial acetic acid in red, glossy, filamentous needles; it melted at $244\text{--}246^\circ$, and dissolved in concentrated sulphuric acid to a deep red solution:

0.1147 gave 12.3 c.c. N_2 at 19° and 758 mm. $\text{N} = 12.30$.

$\text{C}_{17}\text{H}_{15}\text{O}_3\text{N}_3\text{S}$ requires $\text{N} = 12.31$ per cent.

We desire to express our thanks to the Government Grant Committee of the Royal Society and the Research Fund Committee of the Chemical Society for grants which have partly defrayed the expenses of this investigation.

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VII.—*The Action of Hydrogen Dioxide on Thiocarbamides.*

By EDWARD DE BARRY BARNETT.

THE action of hydrogen dioxide on thiocarbamide in oxalic acid solution was investigated by Storch (*Monatsh.*, 1890, **11**, 452), who obtained a salt of the disulphide, $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{S}\cdot\text{S}\cdot\text{C}(\text{NH}_2)\cdot\text{NH}$, but was unable to isolate the free base. Storch also obtained salts of this disulphide by oxidising thiocarbamide with nitric acid and other acid oxidising agents. Evidently in this case the thiocarbamide reacts in the pseudo-form. It occurred to the author to investigate the action of hydrogen dioxide on thiocarbamide in neutral or alkaline solution, as it seemed possible that in these circumstances it might react as a symmetrical diamide.

Oxidation of Thiocarbamide.

Fifteen grams of finely-powdered thiocarbamide were slowly added during an hour to 230 c.c. of 6 per cent. aqueous hydrogen

dioxide, the whole being cooled by surrounding with ice. The thiocarbamide dissolved, and after an hour the oxidation product crystallised in colourless needles. These were extracted with boiling alcohol to remove any unchanged thiocarbamide, and were dried in a vacuum over concentrated sulphuric acid. The yield was 9 grams:

0.3400 gave 0.1387 CO_2 and 0.1103 H_2O . $\text{C}=11.13$; $\text{H}=3.62$.

0.5125 „ 0.2077 CO_2 „ 0.1850 H_2O . $\text{C}=11.05$; $\text{H}=3.82$.

0.1465 „ 0.3225 BaSO_4 . $\text{S}=30.17$.

0.2077 „ 45.4 c.c. N_2 (moist) at 12° and 762 mm. $\text{N}=26.2$.

0.0736, in 20.10 water, gave $\Delta t = -0.072^\circ$. $\text{M.W.}=96$.

$\text{CH}_4\text{O}_2\text{N}_2\text{S}$ requires $\text{C}=11.11$; $\text{H}=3.70$; $\text{S}=29.63$;

$\text{N}=25.9$ per cent. $\text{M.W.}=108$.

From the analytical results, it is clear that Storch's disulphide is not formed under these conditions, and the molecular weight determination shows that condensation does not take place, but that each molecule of thiocarbamide takes up two atoms of oxygen. The compound has faintly acidic properties, and it does not reduce metallic salts, as would be probable if it had the structure $\text{OH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}\cdot\text{OH}$. Further, the ease with which it evolves sulphur dioxide on heating points to the oxygen being in direct union with the sulphur. It was also found that carbamide does not yield a similar compound.

It would appear, therefore, that its constitution is to be represented as $\text{NH}\cdot\text{C}(\text{NH}_2)\cdot\text{SO}_2\text{H}$, and, in order to confirm this, attempts were made to obtain a similar compound from thio-benzamide and thioacetamide, but these were not successful, a mixture of the amide and the unchanged thioamide being the invariable result.

Aminoiminomethanesulphinic acid melts and decomposes at 144° . It is fairly soluble in cold water, to which it imparts a faintly acid reaction, but is insoluble in organic solvents. It decomposes slowly at 100° and rapidly at 110° , sulphur dioxide being evolved. It is rapidly decomposed by boiling water, and from the solution thus obtained chloroplatinic acid precipitates an orange-red salt. This is probably formamidine platinichloride, but it has not been possible to obtain it in sufficient quantity for analysis. Aminoiminomethanesulphinic acid instantly reduces acid permanganate in the cold, and quantitative experiments showed that in doing so it takes up one atom of oxygen. Attempts to isolate this oxidation product failed. On treatment with excess of permanganate, hydrogen cyanide is evolved. It was not found possible to prepare an acetyl derivative by treatment with acetyl chloride.

The investigation was extended to some of the derivatives of thiocarbamide in the hope of obtaining similar compounds which would yield more definite decomposition products.

Oxidation of Allylthiocarbamide.

Ten grams of finely-powdered allylthiocarbamide were gradually added during an hour to 110 c.c. of a 6 per cent. aqueous solution of hydrogen dioxide at 0°. The clear solution was evaporated almost to dryness in a vacuum over concentrated sulphuric acid, and the oily residue extracted with warm alcohol. The filtered solution was evaporated in a vacuum at the ordinary temperature, and the resulting colourless crystals were dried over concentrated sulphuric acid:

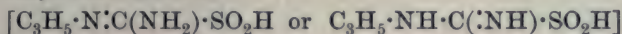
0.2449 gave 0.2626 CO₂ and 0.1206 H₂O. C = 29.24; H = 5.47.

0.2615 „ 0.2782 CO₂ „ 0.1253 H₂O. C = 29.01; H = 5.32.

0.2558 „ 0.3556 BaSO₄. S = 19.09.

C₄H₈O₂N₂S.H₂O requires C = 28.92; H = 6.02; S = 19.27 per cent.

This *allyl* derivative



tends to form a viscous oil, which only crystallises with the utmost difficulty, and hence was not obtained in a state of purity. It melts and decomposes at 165—170°.

Attempts were also made to prepare the substance in the pure condition by oxidising allylthiocarbamide in acetone solution with the calculated amount of aqueous 30 per cent. hydrogen dioxide. On evaporating the acetone in a vacuum, an oil was obtained, which did not crystallise after remaining under anhydrous ether for six weeks.

All attempts to obtain a pure product by oxidising phenylthiocarbamide, either in aqueous or in acetone solution, with hydrogen dioxide yielded a viscous oil which did not crystallise.

The ease with which the oxidation of thiocarbamides takes place seems to depend on the number of substituents present. Thus, with thiocarbamide itself, the action of hydrogen dioxide is violent, and must be carried out at a low temperature; with allylthiocarbamide and phenylthiocarbamide, the reaction is much less violent; and hydrogen dioxide has no action on thiocarbanilide. This is probably to be attributed to the influence of the substituents in hindering the formation of the pseudo-form.

VIII.—*The Influence of Non-electrolytes on the Solubility of Carbon Dioxide in Water.*

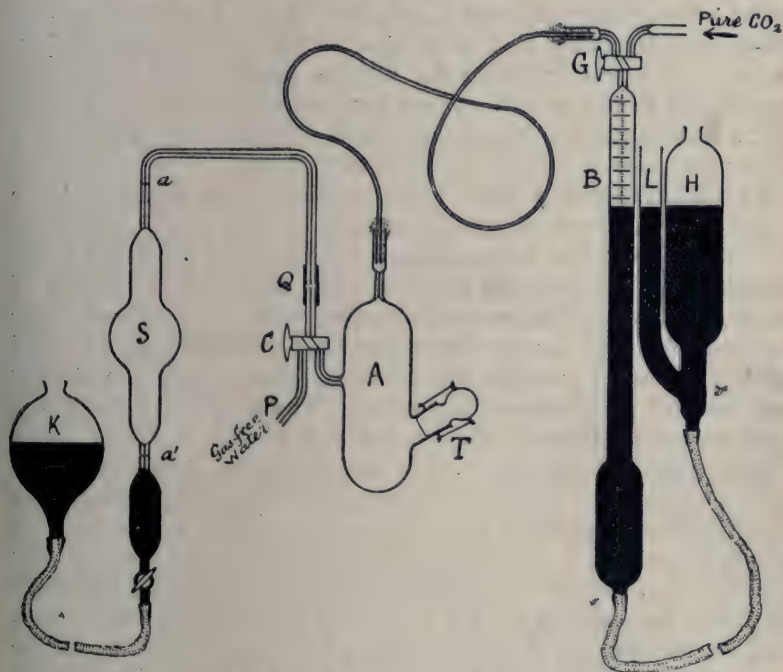
By FRANCIS LAWRY USHER.

THE object of the investigation to be described in this paper was to place upon record a larger number of accurate measurements of the solubility of a gas in solutions of non-electrolytes than has hitherto been available. Although there is a considerable mass of experimental data relating to the solubility of gases in salt solutions, the non-electrolytes examined have been confined to some sugars, chloral hydrate, carbamide, and a few slightly dissociated organic acids (Roth, *Zeitsch. physikal. Chem.*, 1897, **24**, 114; Braun, *ibid.*, 1900, **33**, 721; Knopp, *ibid.*, 1904, **48**, 97; Christoff, *ibid.*, 1905, **53**, 321; Hüfner, *ibid.*, 1906, **57**, 611; Steiner, *Wied. Annalen*, 1894, **52**, 275). The experiments recorded here were all carried out at 20°, and, except in the case of sucrose, at only one concentration, namely, semi-normal. The gas used was carbon dioxide, chosen because its comparatively large absorption-coefficient permitted greater accuracy in the determinations, whilst at the same time its slight deviation from Henry's law is not sufficient to preclude its use as an indifferent gas. The substances studied were sucrose, dextrose, mannitol, glycine, pyrogallol, quinol, catechol, resorcinol, carbamide, thiocarbamide, urethane, acetamide, antipyrine, acetic acid, and *n*-propyl alcohol.

EXPERIMENTAL

Except in the case of the two liquid substances examined, namely, acetic acid and *n*-propyl alcohol, the solutions were of exactly semi-normal strength, and were prepared in the absorption vessel itself. The apparatus was designed with this end in view, and a description of it will now be given. The carbon dioxide was prepared in an ordinary Kipp's apparatus, from marble which had been boiled for some time in distilled water in order to remove adhering and occluded air, and concentrated hydrochloric acid. The gas was found to contain less than 0.03 per cent. of foreign gas. The outlet tube from the Kipp's apparatus was connected through a tap with a large U-tube filled with marble chips, which served to prevent any acid spray from being carried over with the carbon dioxide. The gas was next led through a wash-bottle containing concentrated sulphuric acid, and finally through a phosphoric oxide tube. Wherever practicable, connexions between glass portions of the apparatus were made by sealing the glass together with a

mouth-blowpipe; in fact, the number of taps and rubber connexions was kept as small as possible, and the latter, when it was necessary to use them, consisted of short pieces of pressure tubing of small bore, inside of which the glass ends were brought together. The tap of the Kipp's apparatus was left permanently open, so that the internal gas pressure was always in excess of the atmospheric, and no air could leak into the apparatus. The measuring burette (*B*) was of 100 c.c. capacity. Of this, 50 c.c. were contained in the narrow upper part, which was graduated in tenths of a c.c., and was calibrated by weighing out mercury, whilst the



remaining 50 c.c. were contained in a bulb blown below this graduated portion. The burette was connected by rubber tubing with a mercury reservoir *H*, carrying a levelling tube *L* of the same diameter as the graduated part of the burette, and was provided at the top with a three-way tap *G*, by means of which it could be connected either with the carbon dioxide supply or with the absorption vessel. The absorption vessel *A* was of about 220 c.c. capacity, and was provided near the bottom with a tubulure *T*, about 14 mm. wide, carrying two small glass hooks, and which could be closed by a ground glass stopper carrying a second pair

of hooks, by means of which it could be held firmly in position with two elastic bands. The solid substance was introduced through this tubulure. On the opposite side, and nearer the top, was a short capillary tube carrying a three-way tap *C*, so arranged that either the absorption vessel could be connected with a vessel *S* delivering a known volume of gas-free water, or the latter could be connected, independently of the absorption vessel, with the store of gas-free water employed.

A flexible copper capillary, 2 metres long and of 1.5 mm. bore, was used to connect the absorption vessel with the burette, and was cemented into the glass tubing with marine glue, the junctions being subsequently enclosed in plaster-of-Paris blocks, to prevent them from becoming loose when the absorption vessel was shaken. A thermostat was employed for all the experiments, which were carried out at $20^{\circ} \pm 0.02^{\circ}$. When the room-temperature rose above 20° , a cooling coil was introduced into the thermostat. The method of carrying out a determination is as follows:

In the first place, a semi-normal solution of the substance to be examined was prepared, and its specific gravity at 20° was determined, and from this was calculated the weight of substance which would give a semi-normal solution when dissolved in 117 c.c. of water, this being the amount of water used in every case. The exact quantity of the substance was then weighed into the dried absorption vessel through the tubulure, after which the stopper was inserted and fastened in position. The absorption vessel was now connected through the three-way tap with a Töpler pump and completely exhausted. After closing the tap, it was filled with pure dry carbon dioxide by alternately filling the burette from the supply and allowing the gas in the burette to pass into the absorption vessel, by suitably turning the three-way tap *G*. The absorption vessel was now placed in the thermostat and left there until the temperature of the contained gas was constant at 20° , and it was arranged that when it was full of gas at 20° under the atmospheric pressure, the level of the mercury should be near the top of the burette. The burette reading was then observed, and the room-temperature and barometric height noted. Pure gas-free water had now to be introduced. Ordinary distilled water was used, and was previously boiled out in a vacuum in a round-bottomed flask provided with a rubber stopper carrying two glass tubes, one short, the other passing to the bottom of the flask. As soon as all air had been completely removed, the flask was closed, cooled to a little below 20° , and the longer tube was then connected with the branch *P* of the three-way tap *C*, and so with the vessel *S*, which was filled with mercury, and of which the volume between

two marks on the capillary stem at a and a' was accurately known: this was 117.0 c.c. at 20° . By suitable manipulation all air was removed from the capillary tubing, and the tap C was now turned and the vessel S filled with gas-free water to the lower mark a' . C was next turned in the other direction, and by raising the reservoir K and lowering the reservoir H , the exact quantity of water contained between a and a' was driven into the absorption vessel. C was now closed, and the absorption vessel disconnected at P and Q and placed in the thermostat. It was then shaken vigorously until all the solid was dissolved, and the resulting solution saturated with carbon dioxide at 20° under the atmospheric pressure. When the burette reading was constant, the barometer height and room-temperature were again noted, and the determination was now finished. Care was taken that no gas or liquid passed back from the absorption vessel to the burette, consequently the gas in the burette was always dry, whilst that in the absorption vessel was only dry at the commencement of the experiment. For the purposes of calculation the volume, and hence the densities of the solid substances, had to be known. The values of some of these were taken from papers by Schrödter (*Ber.*, 1879, **12**, 1611; 1880, **13**, 1070), and some were redetermined.

The absorption-coefficients for the liquids, acetic acid and *n*-propyl alcohol, were determined by Ostwald's method in an absorption vessel containing 246.3 c.c. Since the volume of gas absorbed in the case of these liquids was much greater than the capacity of the burette, the latter had to be refilled several times. Although the error of reading was repeated as often as the burette was filled, the volume of gas dealt with was proportionately larger, and the probable error in the final result therefore remained the same as for the other solutions, for which a single filling of the burette sufficed.

Two determinations were carried out with every solution examined, and four in the case of water. The maximum difference between the results of two such experiments was 1 in 250, whilst most agreed to within 1 or 2 in 1000.

Calculation of Results.

The absorption-coefficients (α) given represent the volume of carbon dioxide, reduced to 0° and 760 mm., which is dissolved by 1 c.c. of liquid at 20° when the partial pressure of the carbon dioxide is 760 mm.

(i) Calculation of absorption-coefficient for solutions of solids:

Let x = volume of absorption vessel up to beginning of copper capillary,

- Let y = volume from beginning of copper capillary to mark "0" on burette.
 „ b_1 and b_2 = initial and final burette readings.
 „ A = volume of solution.
 „ a = volume of solid substance,
 „ P = barometric height, corrected to 0° .
 „ p = vapour pressure of solution at 20° .
 „ t = room-temperature.

The corrected initial volume of gas in the apparatus will be

$$\frac{P}{760} \left\{ (x-a) \cdot \frac{273}{293} + (b_1+y) \cdot \frac{273}{273+t} \right\},$$

and the corrected final volume will be:

$$\left\{ \frac{P-p}{760} (x-A) \cdot \frac{273}{293} + \frac{P}{760} (b_2+y) \cdot \frac{273}{273+t} \right\},$$

hence the volume dissolved by A c.c. of the solution

$$= \frac{P}{760} \cdot \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} \left\{ \frac{P}{760} (x-a) - \frac{P-p}{760} (x-A) \right\} \text{c.c.},$$

and

$$a = \frac{\frac{P}{P-p} \cdot \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} \left\{ \frac{P}{P-p} (x-a) - (x-A) \right\}}{A}.$$

If the room-temperature is itself 20° , the expression simplifies to:

$$a = \frac{\frac{273}{293} \left\{ \frac{P}{P-p} (x-a+b_1-b_2) - (x-A) \right\}}{A}.$$

(ii) When water is used instead of a solution of a solid, if W is the volume of water taken:

$$a = \frac{\frac{P}{P-p} \left\{ \frac{273}{273+t} (b_1-b_2) + \frac{273}{293} x \right\} - \frac{273}{293} (x-W)}{W},$$

or

$$a = \frac{\frac{273}{293} \left\{ \frac{P}{P-p} (b_1-b_2+x) - (x-W) \right\}}{W}.$$

if the room-temperature is 20° .

(iii) In the case of the solutions of liquids examined, the absorption-coefficient, measured in the Ostwald vessel, is equal to:

$$\frac{\frac{P}{P-p} \cdot \frac{273}{273+t} \left\{ \Sigma(b) - \Sigma(b') \right\} - \frac{273}{293} W}{A}$$

where b and b' are the burette readings before and after intro-

ducing the gas into the absorption vessel, and W is the volume of solution run out from the absorption vessel.

Nature and Magnitude of Errors.

In all the experiments, an accuracy of 1 in 1000 was aimed at, and the values of α given may be taken as correct to 1 in 500. Since the measured volume difference between the first and last readings was always about 100 c.c., an error of 0.1 c.c. involves an error of 1 in 1000 in the value of α . By far the most important sources of error were (1) inexact levelling when reading the volume of gas in the burette, and (2) variations in the temperature of the thermostat.

There was no difficulty in reading the burette with a maximum error of 0.05 c.c., but the exact adjustment of the levelling tube was not so easy. In the initial reading, when the volume of gas in the apparatus is about 225 c.c., an error of 1 mm. in the levelling involves an error of about 0.33 c.c. In the final reading, when the volume of gas is only half as great, a similar error in levelling involves an error of 0.17 c.c. The actual uncertainty of levelling was probably about a quarter of a millimetre, and if the errors in the two readings were additive, this involves an error of 1.2 in 1000 in the value of α . Thus the probable error introduced by this inaccuracy is 0.6 in 1000.

Variations in temperature affect the results in two ways. Thus, if the temperature of the thermostat is not exactly 20° , not only is the volume of gas soluble in the liquid changed by expansion or contraction, but the absorption-coefficient is also directly influenced. Supposing that at the initial reading the true temperature in the thermostat is $(20 - \theta)^\circ$, and at the final reading it is $(20 + \theta)^\circ$, it can be calculated that the difference between the true and the apparent volume of gas absorbed is:

$$\beta + \frac{27300\theta}{293^2 + 293\theta} + \frac{60060\theta}{293^2 - \theta^2} \text{ c.c.,}$$

where β is the difference between the volume of gas soluble in the liquid at 20° and the volume soluble at $(20 + \theta)^\circ$. This expression, after neglecting θ and θ^2 in the denominator, and evaluation of β from the temperature-coefficient of solubility of carbon dioxide in water, is equal to about 4θ c.c. Now the maximum variation (2θ) in the temperature of the thermostat was 0.04° , and the maximum error from this cause is therefore 0.08 c.c., that is, about 0.8 in 1000.

Compared with the above, the other errors are unimportant. The barometer was read with an accuracy of 0.1 mm., and the height of the mercury column was corrected for expansion from

0° to the room-temperature. The time interval between the initial and final readings was usually about half an hour, and no sensible error was introduced through employing the mean of the two barometer readings, since these never differed by more than 0.2 mm., and could not as a rule be detected. Similarly, the room-temperature was always sufficiently constant during an experiment to preclude the introduction of any appreciable error through employing the mean temperature for the calculations. There is no doubt that the gas in the absorption vessel was completely saturated with water vapour at the second reading, on account of the vigorous shaking which always took place, or that the gas in the burette was dry, since the burette tap was always closed while the absorption vessel was being shaken, and gas was never allowed to pass from the latter into the burette. As already stated, two determinations were made in every case, in which the average difference is 1.7 in 1000, and consequently the probable accuracy of the results is about 1 in 1000.

Results.

Absorption-coefficient in Water.—Four determinations were made, and the values found were (i) 0.8775; (ii) 0.8766; (iii) 0.8755; (iv) 0.8766; mean, 0.877.

This value is in good agreement with that given by Bohr (*Wied. Annalen*, 1899, **68**, 503), namely, $\alpha_{20^\circ} = 0.878^\circ$.

Table I gives the absorption-coefficients (α') in the solutions of sucrose examined, and the specific gravities of the solutions at 20°.

TABLE I.

Concentration.	α' .	Mean α' .	Sp. gr.
$N/8$	$\begin{cases} 0.8465 \\ 0.8449 \end{cases}$	0.846	1.01518
$N/4$	$\begin{cases} 0.8161 \\ 0.8140 \end{cases}$	0.815	1.03125
$N/2$	$\begin{cases} 0.7554 \\ 0.7563 \end{cases}$	0.756	1.06372
N	$\begin{cases} 0.6491 \\ 0.6496 \end{cases}$	0.649	1.12809

In table II are given the absorption-coefficients in semi-normal solutions of the other substances examined, and, for purposes of reference, the specific gravities of the solutions at 20° and the specific gravities of the solid substances at the same temperature.

TABLE II.

Substance.	α' .	Mean α' .	Sp. gr. N/2-solution.	Sp. gr. solid.
Dextrose.....	{0.7914 0.7928	0.792	1.0328	1.56 *
Mannitol.....	{0.7822 0.7811	0.782	1.03031	1.46 *
Glycine	{0.8425 0.8443	0.843	1.01413	1.61 *
Pyrogallol	{0.8529 0.8545	0.853	1.01718	1.45
Quinol.....	{0.8855 0.8876	0.887	1.00946	1.33
Resorcinol	{0.9002 0.9024	0.901	1.00958	1.27
Catechol	{0.8676 0.8692	0.868	1.0107	1.34
Urethane	{0.8690 0.8682	0.869	1.0037	0.99
Carbamide	{0.8634 0.8640	0.864	1.00715	1.33 *
Thiocarbamide	{0.8604 0.8581	0.859	1.00917	1.42 *
Antipyrine	{0.8584 0.8600	0.859	1.01339	1.19 *
Acetamide	{0.8790 0.8785	0.879	1.0005	1.56
Acetic acid	—	0.868	1.0026	—
n-Propyl alcohol ...	—	0.869	0.9939	—

* Redetermined.

Discussion of Results.

Since any theoretical deductions from the results must depend on the way in which the latter are expressed, it is first of all desirable to consider briefly the methods which are usually employed for this purpose. In order to compare together a number of different substances with respect to their influence on the solubility of a third substance, it is, of course, only permissible to employ solutions of the same molecular concentration. Here the usual difficulty arises with regard to the calculation of molecular concentration (compare Abegg, *Zeitsch. physikal. Chem.*, 1894, 15, 248). The semi-normal solutions used in this investigation all contained half a gram-molecule in a litre of the solution, and this concentration is in many cases considerably different from that of a solution containing the same weight of substance in 1000 grams of water. Except in the case of sucrose, no experiments with several different concentrations were carried out, but the figures for this substance certainly suggest that the volume-normal is more convenient for our present purpose than the weight-normal method of calculation, and also that solutions of semi-normal

strength are still sufficiently dilute to permit inferences which may be applied without serious error to very dilute solutions.

In table III are given values for the molecular depression of solubility calculated according to the volume-normal and weight-normal methods for solutions of sucrose. α and α' denote the absorption-coefficients of carbon dioxide in pure water and the solution respectively, N is the number of gram-molecules of sucrose in 1 litre of solution, and N' the number in 1000 grams of water.

TABLE III.

N .	$\alpha - \alpha'/N$.	$\alpha - \alpha'/N'$.
0.125	0.248	0.241
0.25	0.248	0.234
0.5	0.242	0.216
1.0	0.228	0.180

It will be seen from these figures that the molecular depression, calculated by the volume-normal method, is constant for solutions up to $N/4$, and is very little different for those of $N/2$ -concentration; and since sucrose produces a much greater effect than any of the other substances examined, the deviations in the case of these must be still smaller. The purely empirical formula, $\alpha - \alpha'/N^2$, suggested by Jahn for expressing the relation between depression of solubility and concentration in the case of electrolytes, is obviously unsuitable for sucrose, and Roth (*Zeitsch. physikal. Chem.*, 1897, **24**, 114) has shown that the figures for glycerol are better represented by the linear formula.* It is therefore probably safe to assume that for moderately dilute solutions of non-electrolytes the effect on the solubility of carbon dioxide, or of any indifferent slightly soluble third substance, is directly proportional to the amount of non-electrolyte present. It now remains to consider certain attempts at generalisation in the light of the experimental data recorded in this paper.

One of the most recent of such attempts is that of Philip (*Trans.*, 1907, **91**, 711), who suggests that substances which have no tendency to combine with the solvent are without influence on the solubility of an indifferent gas, whilst those which do influence the solubility do so because they remove a portion of the solvent by forming compounds with the latter. By "solubility" is here meant the amount of gas dissolved by unit mass of the pure solvent. For example, the absorption-coefficient of hydrogen in an aqueous solution of chloral hydrate is smaller than in pure water (Knopp, *Zeitsch. physikal. Chem.*, 1904, **48**, 97), but the amount dissolved

* It should be mentioned that Geffcken (*Zeitsch. physikal. Chem.*, 1904, **49**, 257) has pointed out sources of error in the experiments of Gordon, Roth, and Braun, which may invalidate the apparent support they afford to Jahn's empirical formula.

by 1000 grams of water is the same in each case. This statement is not true, however, for solutions of sucrose; and in order to bring this substance into line, it is assumed that the statement would be true if it were not that a certain fraction of the water is withdrawn by the sucrose, and the average number of water molecules attached to one molecule of sucrose is calculated in a way consistent with the theory. This method of calculation involves three assumptions: it presupposes (1) that hydrates are formed, (2) that the gas is insoluble in the dissolved substance, and (3) that it is insoluble in the hydrate.

That such assumptions as these have little foundation in fact may be inferred from the following table, which shows the volume of carbon dioxide dissolved by 1000 grams of pure water for the different semi-normal solutions examined, calculated on the assumption that the water alone is responsible for the absorption of gas observed.

TABLE IV.

Solution.	Carbon dioxide dissolved by 1000 grams of water, in c.c.	Solution.	Carbon dioxide dissolved by 1000 grams of water, in c.c.
Water	878	Catechol	808
Sucrose	797	Urethane	907
Dextrose	841	Carbamide	884
Mannitol	833	Thiocarbamide ...	885
Glycine.....	864	Antipyrine	935
Pyrogallol	894	Acetamide	906
Quinol	928	Acetic acid	893
Resorcinol	945	n-Propyl alcohol...	902

It is noticeable, in the first place, that in eleven out of the fifteen solutions examined a larger quantity of carbon dioxide is dissolved than can be accounted for if the water only is responsible for the absorption. This fact alone suffices to show that if we wish to express the solvent properties of these solutions in terms of the properties of their components, any conclusions depending on the assumption that the dissolved substance has no solvent power are worthless.

It is instructive also to compare, from the point of view of the hydrate theory, the behaviour of some of these substances with that of the solutions used by Jones and Getman (*Amer. Chem. J.*, 1904, **32**, 308) in their cryoscopic investigations. If the "average molecular hydration" is calculated in the way described by Philip from the figures given above for sucrose, dextrose, and mannitol, we arrive at the conclusion that sucrose is hydrated to the extent of 3.6 molecules of water, dextrose 4.6 molecules, and mannitol 5.2 molecules—values which are completely at variance with those deduced by Jones and Getman from their data for the molecular

depression of the freezing point. These authors conclude that sucrose in semi-normal solution at 0° forms complexes containing about 5 molecules of water, whereas dextrose is hydrated only to a small extent, and the tendency of mannitol to form hydrates is insignificant. It is not intended here to dispute the existence of hydrates in solution, but it may be permissible to raise the question whether much is to be gained by referring abnormal depression of solubility to this cause, when by so doing it becomes necessary to make other and more improbable assumptions.

Of a different character is the generalisation deduced, on thermodynamic principles, by Jahn (compare Roth, *Zeitsch. physikal. Chem.*, 1897, **24**, 115). According to this, the molecular concentration of a gas remains the same when it is dissolved to saturation in a dilute solution of an indifferent non-volatile substance as when it saturates the pure solvent under the same conditions of temperature and pressure. In other words, if C_1 denotes the ratio of the number of gas-molecules to the sum of the molecules of gas and solvent, and C_2 is the ratio of gas-molecules to the sum of those of gas, solvent, and third substance, the theory requires that C_1/C_2 shall be equal to unity, provided that the following conditions are fulfilled: (i) The gas must exert no chemical action on the solvent or the solution; (ii) it must have the same molecular weight in the liquid as in the gas phase; (iii) the solution must be dilute.

In a limited number of cases, results have been obtained which are described as being in good agreement with the theory. Thus, Roth (*loc. cit.*), using nitrous oxide, found $C_1/C_2 = 1.009$ for carbamide at about semi-normal concentration, 1.013 for glycerol, and 1.009 for oxalic acid. Braun (*loc. cit.*) found 1.037 for carbamide and 1.023 for propionic acid in the case of nitrogen; and, in the case of hydrogen, 1.015 for propionic acid. Knopp (*loc. cit.*) found for chloral hydrate, when hydrogen was used, 0.993, and when nitrous oxide was used, the ratio was 1.010 for chloral hydrate and 1.037 for propionic acid.

Here we have values of C_1/C_2 deviating by anything between 0.7 and 3.7 per cent. from the theoretical value; but in view of the fact that the actual change of solubility effected lies between the limits 1.3 and 4.5 per cent., it becomes obvious that the apparently good agreement has no significance whatever. It should be mentioned that Knopp's experiments were all carried out at 20° , whilst those of Roth and Braun were carried out at 5° , 10° , 15° , 20° , and 25° . The figures quoted above refer to the mean of the results obtained at these five temperatures; the actual value of C_1/C_2 was found to diminish with rising temperature.

In table V the values of C_1/C_2 for the substances employed in the present investigation are tabulated, and it is interesting to compare the percentage deviations from the theory, given in the third column, with the percentage change in solubility of the gas brought about by the non-electrolytes used, given in the fourth column.

TABLE V.

Solution.	C_1/C_2 .	Percentage deviation from $C_1/C_2 = 1$.	Percentage change of solubility.
N-Sucrose	1·101	10·1	26·0
N/8-Sucrose	1·012	1·2	3·5
N/4-Sucrose	1·024	2·4	7·1
N/2-Sucrose	1·048	4·8	13·8
N/2-Dextrose	1·056	5·6	9·7
N/2-Mannitol.....	1·065	6·5	10·8
N/2-Glycine	1·026	2·6	3·9
N/2-Pyrogallol	0·9921	0·8	2·7
N/2-Thiocarbamide ...	1·002	0·2	2·0
N/2-Carbamide	1·003	0·3	1·5
N/2-Urethane.....	0·9789	2·1	1·0
N/2-Antipyrine	0·9494	5·1	2·0
N/2-Catechol	0·9762	2·4	1·0
N/2-Quinol	0·9554	4·5	1·0
N/2-Resorcinol	0·9396	6·1	2·7
N/2-Acetamide	0·9795	2·1	0·2
N/2-Acetic acid	0·9936	0·6	1·0
N/2-n-Propyl alcohol.	0·9817	1·8	1·0

It will be seen from this table that in no less than seven instances the deviation from the theory actually exceeds the magnitude of the effect which is being studied; and, in general, the extent of the discrepancy increases with the amount of the effect produced. There can, however, be no doubt that the formula deduced by Jahn is inapplicable to the experimental data hitherto available; in other words, that the conditions for which the formula is valid are not fulfilled in the experiments. Indeed, the influence of most non-electrolytes is so small that it may reasonably be doubted whether a rigid confirmation of the theory is possible with our present methods of determining gas-solubility; and in any case there is the possibility that the dissolved substance, although chemically indifferent, may itself be capable of dissolving the gas employed.

An attempt has been made by Roth (*Zeitsch. physikal. Chem.*, 1903, **43**, 539) to find some common factor which will bring the deviations from Jahn's thermodynamic formula into line with deviations from van't Hoff's freezing-point law, and it was shown that a parallelism did exist in the cases of glycerol and sucrose, both of which give too large a depression of the freezing point, and too great a value for C_1/C_2 . Thiocarbamide and glycine, however, give too small depressions, whereas the values of C_1/C_2

for these substances are respectively 1.002 and 1.026 in semi-normal solution at 20°, and would, of course, be greater still at 0°.

It seems, therefore, that the effect on the solubility of a gas* produced by non-electrolytes is not capable of explanation by reference either to the formation of hydrates in solution or to deviations from the theory of osmotic pressure—conclusions which have already been expressed by Levin (*Zeitsch. physikal. Chem.*, 1906, **55**, 513); but that since these effects are, as Geffcken (*loc. cit.*) has shown, practically independent of the solubility of the gas and almost entirely determined by the nature of the solvent or solution, it is only possible at present to refer them to mutual interaction among the molecules. It only remains to be mentioned that the last-named author has already called attention to a parallelism which exists between depression or elevation of solubility and such properties as compressibility and surface tension, and it is possible that the whole problem might be more successfully attacked from this point of view.

This research was carried out at the suggestion of Prof. Rothmund, to whom I am greatly indebted for much kindly advice and criticism, as well as for placing at my disposal the necessary apparatus and material.

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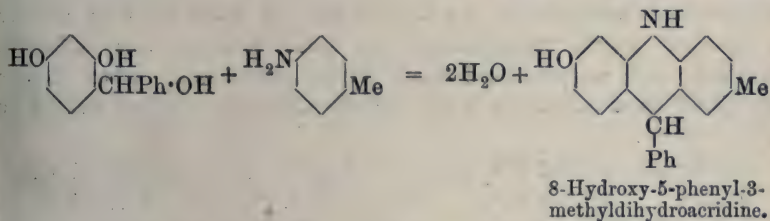
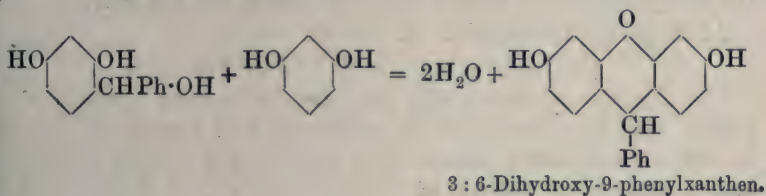
IX.—*The Condensation of Benzaldehyde with Resorcinol.*

By FRANK GEORGE POPE and HUBERT HOWARD.

THE reaction between benzaldehyde and resorcinol has apparently been very little studied. Michael (*Amer. Chem. J.*, 1884, **5**, 338), by the addition of small quantities of hydrochloric acid to an alcoholic solution of the two reacting substances, obtained a resin to which he assigned the empirical formula $C_{26}H_{20}O_4$. This substance yielded a tetra-acetate, and also, on treatment with more acid, was converted into a crystalline isomeride. Liebermann and Lindenbaum (*Ber.*, 1904, **37**, 1171), by heating an alcoholic solu-

* And also of a slightly soluble salt (compare Rothmund, *Zeitsch. physikal. Chem.*, 1909, **69**, 523).

tion of the two components with concentrated sulphuric acid, obtained a compound having the composition $C_{13}H_{10}O_3$, which on acetylation yielded a triacetate. Since the above method of procedure was, to all intents and purposes, unproductive, it occurred to us that by using Manasse's method of condensation (*Ber.*, 1894, **27**, 2409) the two reacting components might yield 2:4-dihydroxybenzhydrol, which would then be of considerable use in the preparation of substituted fluorones and acridines. We have succeeded in obtaining the hydrol, and have condensed it with various phenols and amines and prepared the corresponding xanthenes and dihydroacridines, as typical examples of which may be taken the reaction between the hydrol and resorcinol and the hydrol and *p*-toluidine, thus:



EXPERIMENTAL.

2:4-Dihydroxybenzhydrol, $C_6H_2(OH)_2 \cdot CH(OH) \cdot C_6H_5$.—Twenty-two grams of resorcinol were dissolved in 500 c.c. of water, containing 50 grams of sodium hydroxide, and shaken from time to time with the calculated amount of benzaldehyde (21.2 grams). The solution gradually darkened in colour, and became ultimately deep blood-red, the odour of the benzaldehyde gradually disappearing. The next day the solution was diluted with about its own volume of water, and then acidified with either dilute hydrochloric or acetic acid, when a pale brownish-white, microcrystalline precipitate of the hydrol was obtained. This was collected, well washed with water, redissolved in sodium hydroxide solution, and again precipitated and washed. It is to some extent soluble in alcohol or glacial acetic acid, and more readily so in pyridine, but cannot be recovered in a crystalline form from these solvents. For purposes of analysis, the reprecipitated hydrol was repeatedly

extracted with hot water, collected, and well washed and finally dried in a desiccator over sulphuric acid:

0.1100 gave 0.2916 CO_2 and 0.0585 H_2O . $\text{C}=72.30$; $\text{H}=5.91$.

0.2222 „ 0.5888 CO_2 „ 0.1025 H_2O . $\text{C}=72.27$; $\text{H}=5.13$.

$\text{C}_{13}\text{H}_{12}\text{O}_3$ requires $\text{C}=72.22$; $\text{H}=5.56$ per cent.

2: 4-*Dihydroxybenzhydrol* is a faintly yellowish-coloured substance, which darkens rather rapidly on exposure to air. It does not melt, but chars at about 200° . It is readily soluble in solutions of the alkali hydroxides, the solutions possessing a dark blood-red colour. By dissolving the hydrol in water containing the calculated amount of potassium hydroxide and evaporating the solution to dryness on the water-bath, a red *dipotassium* compound is obtained. On recrystallisation from water, this gave, on analysis:

0.328 gave 0.196 K_2SO_4 . $\text{K}=26.79$.

$\text{C}_{13}\text{H}_{10}\text{O}_3\text{K}_2$ requires $\text{K}=26.69$ per cent.

The *diacetyl* derivative was prepared by heating 5 grams of the hydrol with 25 grams of acetic anhydride and 1 gram of zinc dust for three hours under reflux. The solution was filtered and poured into a mixture of 300 c.c. of water and 50 c.c. of alcohol, and the whole then warmed on the water-bath for some time to remove excess of acetic anhydride. The solid product was collected, washed, and recrystallised from dilute acetic acid, when it was obtained as a colourless solid, which decomposes when heated to about 200° :

0.1092 gave 0.2736 CO_2 and 0.048 H_2O . $\text{C}=68.33$; $\text{H}=4.88$.

0.1042 „ 0.2604 CO_2 „ 0.0466 H_2O . $\text{C}=68.15$; $\text{H}=4.97$.

$\text{C}_{17}\text{H}_{16}\text{O}_5$ requires $\text{C}=68.00$; $\text{H}=5.33$ per cent.

2: 4-*Diacetoxybenzhydrol* is soluble in acetone, chloroform, benzene, or acetic acid, but insoluble in light petroleum.

The *benzoyl* derivative was prepared by dissolving 4.32 grams of the hydrol in the calculated amount of sodium hydroxide (2 mols.) dissolved in 40 c.c. of water, and adding 5.62 grams of benzoyl chloride. The mixture was well shaken, and the pale yellow precipitate collected, washed, and crystallised from dilute acetic acid:

0.1014 gave 0.284 CO_2 and 0.0429 H_2O . $\text{C}=76.38$; $\text{H}=4.70$.

0.2262 „ 0.6372 CO_2 „ 0.096 H_2O . $\text{C}=76.82$; $\text{H}=4.75$.

$\text{C}_{27}\text{H}_{20}\text{O}_5$ requires $\text{C}=76.41$; $\text{H}=4.72$ per cent.

2: 4-*Dibenzoyloxybenzhydrol* is an almost colourless solid, which darkens somewhat on exposure. It is soluble in benzene, chloroform, or acetic acid, but insoluble in light petroleum. On heating, it darkens at about 170° , and melts and decomposes at about 195° .

The *dimethyl ether* was obtained as follows. 4.5 Grams of

potassium hydroxide were dissolved in 50 c.c. of methyl alcohol, 4 grams of the hydrol were added, along with 6 grams of methyl iodide, and the whole was heated under reflux for four hours. The solution was then diluted with water, and rendered just acid. The dark precipitate thus obtained was collected, washed, and crystallised from dilute acetic acid, from which it was obtained as a rather brownish-coloured, microcrystalline solid:

0.093 gave 0.2516 CO_2 and 0.054 H_2O . $\text{C}=73.78$; $\text{H}=6.45$.

0.109 „ 0.294 CO_2 „ 0.062 H_2O . $\text{C}=73.56$; $\text{H}=6.32$.

$\text{C}_{15}\text{H}_{16}\text{O}_3$ requires $\text{C}=73.77$; $\text{H}=6.56$ per cent.

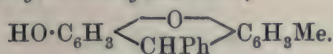
Since the above analyses would not absolutely exclude the possibility that the compound might be a monomethyl ether, $\text{C}_{14}\text{H}_{14}\text{O}_3$, which would require $\text{C}=73.05$, $\text{H}=6.09$ per cent., the methoxyl groups were estimated by the Zeisel method, with the following result:

0.8104 gave 0.162 AgI. $\text{OMe}=26.38$.

$\text{C}_{13}\text{H}_{10}\text{O}(\text{OMe})_2$ requires $\text{OMe}=25.41$ per cent.

2:4-Dimethoxybenzhydrol is soluble in acetone, benzene, or acetic acid. It decomposes when heated above 130° .

6-Hydroxy-9-phenyl-2-methylxanthen,



—Four grams of 2:4-dihydroxybenzhydrol were mixed with 2 grams of *p*-cresol and 4 grams of anhydrous zinc chloride, and the mixture was heated to 170° for four hours. When cold, the product was extracted with hot water several times to remove zinc salts, and finally crystallised from alcohol. It is a red,* crystalline solid, which melts at 112° , and it is readily soluble in alcohol, but sparingly so in acetic acid:

0.111 gave 0.338 CO_2 and 0.057 H_2O . $\text{C}=83.05$; $\text{H}=5.70$.

$\text{C}_{20}\text{H}_{16}\text{O}_2$ requires $\text{C}=83.33$; $\text{H}=5.56$ per cent.

3:6-Dihydroxy-9-phenylxanthen, $\text{HO}\cdot\text{C}_6\text{H}_3\begin{array}{c} \diagup \text{O} \diagdown \\ \text{CHPh} \end{array} \text{C}_6\text{H}_3\cdot\text{OH}$,

is obtained in a similar manner when 4 grams of dihydroxybenzhydrol are heated with 2 grams of resorcinol and 4 grams of anhydrous zinc chloride for four hours to 160° . It crystallises from alcohol in small red* needles, which melt at 136° , and are soluble in alcohol, pyridine, benzene, or glacial acetic acid:

0.1068 gave 0.3075 CO_2 and 0.0475 H_2O . $\text{C}=78.52$; $\text{H}=4.94$.

$\text{C}_{19}\text{H}_{14}\text{O}_3$ requires $\text{C}=78.62$; $\text{H}=4.83$ per cent.

* In this case the colour observed is, in all probability, due to slight oxidation with consequent formation of small quantities of the corresponding fluorone derivatives, the xanthenes being difficult to keep in a state of absolute purity.

3: 6-*Dibenzoyl-9-phenylxanthen* was prepared by the Schotten-Baumann method, and on recrystallisation from dilute alcohol was obtained as a rather reddish-coloured solid, melting and decomposing at 125°:

0.1082 gave 0.3148 CO₂ and 0.0446 H₂O. C=79.35; H=4.58.

C₃₃H₂₂O₅ requires C=79.52; H=4.42 per cent.

A *bromo*-derivative was obtained when the dihydroxyxanthen was dissolved in glacial acetic acid, and the calculated amount of bromine added gradually to the solution. A precipitate was formed at first, but dissolved on adding more of the bromine. After some time the solution was poured into water. The precipitate was collected, washed, dried, and crystallised from amyl acetate, from which it separated in small, red needles. It is soluble in amyl acetate, pyridine, chloroform, or acetic acid, but sparingly so in alcohol, the solution obtained resembling that of eosin in alcohol, and possessing a yellowish-green fluorescence:

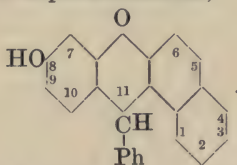
0.15 gave 0.1866 AgBr. Br=52.94.

C₁₉H₈O₃Br₄ requires Br=52.98 per cent.

C₁₉H₁₀O₃Br₄ „ Br=52.80 „

It is most probable that this bromo-compound is *tetrabromo-3-hydroxy-9-phenylfluorone*, C₁₉H₈O₃Br₄, the first action of the bromine being that of an oxidising agent, since an alcoholic alkaline solution of the bromo-compound, on treatment with zinc dust, gives a colourless solution, which rapidly oxidises with the formation of the deep red colour shown by the bromo-derivative in alcoholic alkaline solution.

8-*Hydroxy-11-phenyl-β-naphthaxanthen*,



—4.32 Grams of the hydrol were mixed with 2.88 grams of β-naphthol and 5 grams of anhydrous zinc chloride, and the mixture was heated to 150° for six hours. The zinc salts were extracted with water, and the residue was dissolved in dilute sodium hydroxide solution. Acetic acid was then added, and the precipitate obtained was collected and well washed with water. On recrystallisation from alcohol, the compound separated as a dark red,* crystalline powder, melting at 84°:

0.1124 gave 0.3506 CO₂ and 0.0506 H₂O. C=85.07; H=5.05.

C₂₃H₁₆O₂ requires C=85.18; H=4.94 per cent.

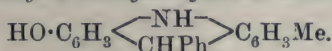
* See footnote, p. 81.

The *benzoyl* derivative (8-benzoyloxy-11-phenyl- β -naphthaxanthen) was prepared by the Schotten-Baumann method, and on recrystallisation from alcohol was obtained in small, almost colourless needles, decomposing when heated to about 103°:

0.103 gave 0.318 CO₂ and 0.046 H₂O. C=84.20; H=4.96.

C₃₀H₂₀O₃ requires C=84.11; H=4.67 per cent.

8-Hydroxy-5-phenyl-3-methyldihydroacridine,



—This substance was prepared by heating 8.64 grams of the hydrol with 4.28 grams of *p*-toluidine and 10 grams of anhydrous zinc chloride for four hours at 160°. The product was then boiled with water and crystallised from dilute alcohol. Owing to the obstinate retention of small traces of zinc salts, it was then found advisable to boil the product again with very dilute hydrochloric acid, filter, well wash, and again recrystallise. The product thus obtained was a light brownish-coloured * powder:

0.1002 gave 0.3082 CO₂ and 0.055 H₂O. C=83.88; H=6.09.

0.115 „ 5.0 c.c. N₂ (dry) at 22° and 761 mm. N=5.04.

C₂₀H₁₇ON requires C=83.62; H=5.92; N=4.88 per cent.

The *benzoyl* derivative (8-benzoyloxy-5-phenyl-3-methyldihydroacridine) was prepared by the Schotten-Baumann reaction. On crystallisation from dilute alcohol it separated in almost colourless needles, which decomposed at about 135°:

0.108 gave 0.3274 CO₂ and 0.0516 H₂O. C=82.67; H=5.31.

0.52 „ 17.4 c.c. N₂ (dry) at 21° and 740 mm. N=3.77.

C₂₇H₂₁O₂N requires C=82.86; H=5.26; N=3.58 per cent.

We are at present engaged on the oxidation of the xanthen and dihydroacridine derivatives, also in the condensation of the substituted benzaldehydes with phenols and amines, and hope to be able to lay the results before the Society later.

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* The colour here again is to be attributed to slight oxidation.

X.—*The Relation between the Strengths of Acids and Bases, and the Quantitative Distribution of Affinity in the Molecule. Part II.*

By BERNHARD FLÜRSCHHEIM.

IN Part I (Trans., 1909, **95**, 718)* it has been shown how the hitherto inexplicable influence which many substituents exercise on the dissociation constants of acids and bases can be approximately foreseen if the electropolar nature of the substituent is taken into consideration, and also the amount of chemical force required for its linking and the steric effect exercised by it on the electrolytic equilibrium. Mention was also made of the fact that all known constants of amines are in harmony with the theory, with the exception of the chloro- and bromo-anilines and *p*-aminophenol. The latter compound and *p*-anisidine will be dealt with in Part III; the present paper is concerned with the halogen-substituted anilines, and, in view of conflicting values given by different authors, also with the toluidines. Further, a graphic method has been devised by which the superposition of the three factors can be better illustrated than by the tabular arrangement previously given. Lastly, an analysis of the constitution of some derivatives of triphenylcarbinol, etc., is intended to demonstrate how these views may be applied with advantage to the elucidation of some disputed problems.

1.—*The Dissociation Constants of p-Toluidine, m-Toluidine, p-Chloroaniline, m-Chloroaniline, p-Bromoaniline, and m-Bromoaniline.*

The following values have been hitherto obtained:

<i>p</i> -Toluidine.....	1.56×10^{-9} (at 25° , $k_w = 1.18 \times 10^{-14}$) (Bredig, <i>Zeitsch. physikal. Chem.</i> , 1894, 13 , 303); 1.13×10^{-9} (at 25° , $k_w = 1.18 \times 10^{-14}$) (Farmer and Warth, Trans, 1904, 85 , 1713); 4.5×10^{-10} (at 15°) (Veley, Trans., 1908, 93 , 2122); 2.2×10^{-10} (at 25°) (Denison and Steele, Trans., 1906, 89 , 999, 1386).
<i>m</i> -Toluidine	5.9×10^{-10} (at 25° , $k_w = 1.18 \times 10^{-14}$) (Bredig, <i>loc. cit.</i>); 2.9×10^{-10} (at 25° , $k_w = 1.18 \times 10^{-14}$) (Farmer and Warth, <i>loc. cit.</i>); 3.9×10^{-10} (at 14°) (Veley, <i>loc. cit.</i>).
<i>p</i> -Chloroaniline ...	1.49×10^{-10} (at 25°) (Farmer and Warth); 1.24×10^{-11} (at 10°) (Veley).

* In Part I, page 727, line 11 from below, the passage "the strength of linkings is more affected . . ." should read "the strength of linkings is less affected . . ." This principle has been correctly applied in the tables. Also page 729, line 3, "0.00158" should read "0.00149." Some printers' errors have been corrected in the list of "Errata."

<i>m</i> -Chloroaniline...	6.58×10^{-12} (at 10°) (Veley).
<i>p</i> -Bromoaniline ...	2.07×10^{-10} (at 18°) (Veley); 1.04×10^{-10} (at 25°) (Farmer and Warth).
<i>m</i> -Bromoaniline...	9.5×10^{-11} (at 19°) (Veley).

All these constants have been determined by hydrolysis, either by electrical conductivity (Bredig), or by an indicator (Veley), distribution (Farmer and Warth), and velocity of migration (Denison and Steele). In addition, hydrolytic values have been determined for some of these bases electrolytically by Walker (*Zeitsch. physikal. Chem.*, 1889, **4**, 319), and colorimetrically by Lellmann and Götz (*Annalen*, 1893, **274**, 139), but no constant has been calculated. According to Walker, the relative strength, beginning with the weakest, is: *m*-chloroaniline, *p*-chloroaniline; *p*-toluidine, aniline, *m*-toluidine, and, according to Lellmann and Götz: *m*-chloroaniline, *m*-bromoaniline, *p*-chloroaniline, *p*-bromoaniline; aniline, *p*-toluidine. After due allowance has been made for the effect of the differing temperatures chosen by Veley, his series would be: *m*-chloroaniline, *p*-chloroaniline, *m*-bromoaniline, *p*-bromoaniline; aniline, *m*-toluidine, *p*-toluidine. The series of Farmer and Warth is: *p*-bromoaniline, *p*-chloroaniline; *m*-toluidine, aniline, *p*-toluidine; and that of Bredig: aniline, *m*-toluidine, *p*-toluidine.

If this mass of contradictory evidence is sifted in the light of the present theory, *m*-toluidine should be stronger than aniline (compare Part I, tables). Similarly, *m*-bromoaniline should be stronger than *m*-chloroaniline, for the same reason that *m*-bromobenzoic acid is weaker than *m*-chlorobenzoic acid (compare Part I, tables). The relative strength of the meta- and para-halogen-substituted compounds is, however, theoretically not quite so simply deduced. It is well known that many substituents exercise a stronger polar influence from the para- than from the meta-position, notwithstanding the greater number of intervening atoms, which, in an open chain, reduce the polar effect of a substituent. This can only be due to a direct neutralisation of residual affinity between the para-atoms, as has been assumed in the benzene formula of Claus. The strength of this diagonal bond is, however, variable, for it depends on the amount of affinity which the carbon atoms of the nucleus have to offer to the substituents. In paramonosubstituted anilines, the diagonal bond between the substituted carbon atoms is the weaker the more unsaturated the substituting atom is, that is, the more affinity it can neutralise. An independent proof for this has been given by means of the directing influence on introduction of a substituent (*J. pr. Chem.*, 1905, [ii] **71**, 502). Whereas steric considerations would lead one to expect that the ratio of para- to ortho-compound would be

greater when bromobenzene than when chlorobenzene is nitrated, the reverse has been observed. It might be argued that this is due to the greater polarity of chlorine, which might inhibit the formation of an ortho-compound; but this view is excluded by the fact that other strongly negative groups, such as NO_2 and CO , which are mainly substituted in the meta-position, always yield more ortho- than para-di-derivatives as by-products. The only explanation that remains is therefore to assume that an unsaturated substituent, like chlorine, by making a great demand on the affinity of the carbon atom to which it is linked, primarily weakens the diagonal bond with the para-atom to a greater extent than the normal bonds with the ortho-atoms, with the result that the free affinity on which substitution depends is more increased in the para- than in the ortho-position; the reverse happens when an oversaturated atom, such as quinquevalent nitrogen in the nitro-group, is linked to the nucleus, which it cannot bind as strongly as the hydrogen atom that it has displaced. Moreover, since chlorine has a stronger para-substituting power, in similar conditions, than bromine, it must reduce the diagonal exchange of affinity to a greater extent, that is, it must be a little more strongly linked to the nucleus, a deduction which is in agreement with other facts and views briefly outlined in a recent preliminary note (Proc., 1909, 25, 261), also with the constants of chloro- and bromo-substituted aliphatic acids (Part I, tables).

If it follows, however, as a necessary deduction from observed facts, that the strength of the diagonal bond is variable, it remained an open question whether the transmission of a polar effect from atom to atom also varies with the amount of affinity bound by their linking. The affinity values of the chloro- and bromo-anilines are capable of supplying an experimental solution. For none of the meta- or para-compounds is there a steric factor to be considered. The quantitative factor would tend to make *p*-nitroaniline a stronger base than the meta-isomeride (Part I, tables); nevertheless, *p*-nitroaniline, where the strong negative influence is transmitted by a strong diagonal bond, is four times weaker than *m*-nitroaniline. On the other hand, taking the quantitative factor alone, the para-halogen-substituted anilines would be weaker than the meta-isomerides. From analogy to the nitroanilines, the polar factor would have the same effect if the transfer of polarity were independent of the strength of the diagonal bond. If, however, that transfer showed a variation parallel to that of the bond, it is conceivable that with a weakening of the diagonal linking, as in *p*-chloroaniline, a point may be reached where the diagonal influence becomes smaller than the

difference between the polar effects in the γ - and δ -positions in an open chain; in that case the polar factor becomes smaller for the para- than for the meta-position, and this difference may again conceivably be so great that it outweighs the quantitative effect in the opposite direction. The result would be that *p*-chloro- and bromo-aniline would be stronger bases than their isomerides. The same considerations enable one to foresee the relative strength of *p*-chloro- and *p*-bromo-aniline in either case. If the polar influence transmitted through a bond is independent of the strength of the latter, chlorine, being a little more strongly linked and also more polar, would, in the para-position, weaken aniline more than would bromine; in the reverse case, the very fact that chlorine is more strongly linked, would, by weakening the diagonal bond, also reduce its polar effect, so that *p*-chloroaniline might become a stronger base than *p*-bromoaniline. Moreover, if the polar factor outweighed the quantitative factor as regards the relative strength of the meta- and para-isomerides, it would have to do the same with regard to that of the para-compounds among each other. In other words, *p*-chloroaniline not only might, but would, be stronger than *p*-bromoaniline if *p*-chloroaniline were stronger than *m*-chloroaniline; the sequence of values of Lellmann and Götz, and of Veley, would therefore be impossible.

To decide these important points, it was necessary to devise a more trustworthy method for the determination of the affinity values of very weak bases. The vastly differing results quoted above show that no such method existed. It is well known that values based on electrical determinations of hydrolysis become less accurate for very weak bases, whereas the colorimetric methods depend greatly on physiological factors, and can claim but a qualitative usefulness. A good distribution method, however, which would yield values in agreement with those obtained by the conductivity method for stronger bases, where the latter method is trustworthy, could also be relied on to give accurate results for very weak bases, where the conductivity method fails. Such a method, simple and suitable also for organic laboratories, would be that due to Farmer and Warth (*loc. cit.*). The results published by these authors for *m*- and *p*-toluidine, however, differ considerably from those obtained by Bredig by the conductivity method (*loc. cit.*). This has been ascribed to association. Having had some experience of the difficulties affecting the quantitative determination of volatile amines, the author thought that the incorrect results of Farmer and Warth might be due either to actual experimental error in the determination of the amines, or to the too high concentrations used, which again may have been necessitated by

the difficulty of accurately estimating small quantities of the amine. As may be seen in the experimental part, this was found to be the case, and the introduction of an accurate method of determining the amine gave results in agreement with the determinations by conductivity where such were available, and closely agreeing with each other in all the other cases. The following values were obtained, at 25° and for $k_w = 1.18$: *m*-toluidine, 5.48×10^{-10} ; *p*-toluidine, 1.48×10^{-9} ; *m*-chloroaniline, 3.45×10^{-11} ; *m*-bromoaniline, 3.82×10^{-11} ; *p*-chloroaniline, 9.9×10^{-11} ; *p*-bromoaniline, 8.8×10^{-11} . The relative values for *m*- and *p*-toluidine and those for *m*-chloro- and *m*-bromo-aniline agree with the theory. The relative values for the meta- chloro- and bromo-compounds on the one hand, for the para-compounds on the other, constitute, on the basis of the present theory, an experimental proof that *atoms transmit their polarity to each other in proportion to the quantitative strength of the bond by which they are linked*. Lastly, the relative values for *p*-chloro- and bromo-aniline also agree with the theory.

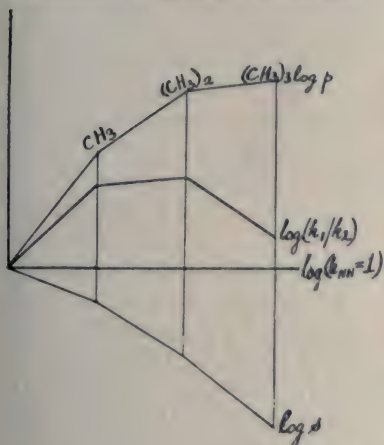
2.—*Graphical Illustration of the Three Factors which Determine the Dissociation Constant.*

When a radicle is introduced two or three times successively in the same position, the magnitude of the effect on each introduction is generally not the same. This is in accordance with the theoretical postulate that all three factors, if they differ from 1, must vary with each substitution. When two atoms A and B are linked, by partly transferring the polarity of each to the other, they reduce the difference in their specific polarities (compare Proc., *loc. cit.*). If a second atom B is then linked to A, the difference of polarity being now less than it was for the first B, the polar effect of the second B on A must be smaller than that of the first B. Similarly, since the force with which atoms are linked is the result of an equilibrium (*J. pr. Chem.*, 1907, [ii], 76, 185; Proc., *loc. cit.*), that equilibrium cannot be displaced so much by the second atom as by the first. The steric factor, on the other hand, shows the reverse change. The behaviour of di-ortho-substituted when compared with mono-ortho-substituted compounds, and that of tertiary, secondary, and primary aliphatic acids on esterification leave no room for doubt that the steric effect is relatively greater for each subsequent introduction of the same substituent in the same position.

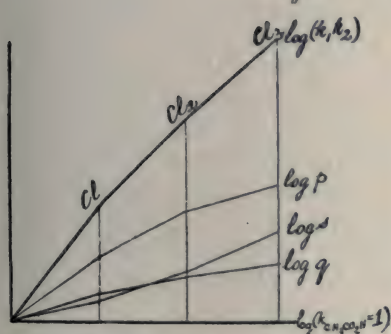
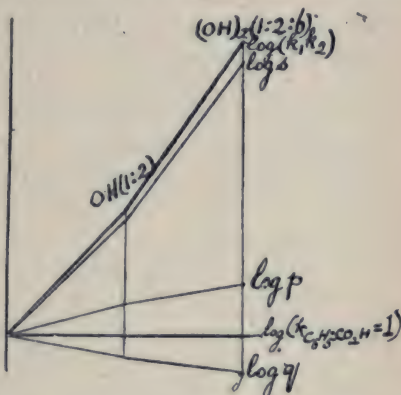
All this has been duly considered in the tables given in Part I, but it can, of course, be much more accurately represented graphically, as exemplified by the accompanying figures. The

logarithms of the factors and the total effect are plotted as ordinates, and the total number of substituting groups as abscissæ; the logarithms of the factors, when added, give the logarithm of the total effect exercised by a substituent. This total is the quotient of the dissociation constant of the substituted by that of the unsubstituted compound. The individual factors, although they cannot, of course, be determined with mathematical accuracy,

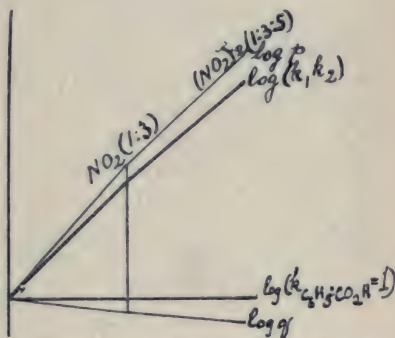
Substitution of Methyl in Ammonia.



Substitution of Hydroxyl in Benzoic Acid.



Substitution of Chlorine in Acetic Acid.



Substitution of NO₂ in Benzoic Acid.

can still be approximately arrived at, especially as regards their relative values, by conforming to the three postulates just mentioned, and by comparing a great number of compounds, and generally conforming to the principles laid down in Part I.

As the curves for ammonia show, the hitherto inexplicable effect of methyl in first raising, then lowering, the constant is readily accounted for. For trichloroacetic acid, the older value by

Ostwald ($K=121$) has been adopted, since the curves obtained with the constant given by Drucker ($K<40$) left no doubt that this value is too low, a conclusion which is supported by comparisons with other chlorinated acids. (Owing to the exigencies of space, the different figures are on different scales.)

3.—*The Constitution and Relative Stability of Some Quaternary Bases, Salts, and Ions.*

The constitution of numerous coloured organic salts is still a much discussed point, the question being generally whether the salts and ions have the same constitution as the corresponding base, or whether the ionisation of the latter has been accompanied by intramolecular rearrangement. In many cases, at least in solution, differences of constitution have been established; but in others only the inconclusive evidence afforded by the colour of the compounds has been available. The present theory suggests the following deductions.

A linking can be broken by ionisation if the amount of affinity available for its formation is relatively small (see Part I), or if the respective atoms are of pronounced and opposite polarity. Now the former of these conditions is common to all organic "halochromic" bases, both in their normal and pseudo-forms. In triphenylcarbinol, for instance, the aliphatic carbon atom of the benzenoid form is to a great extent saturated by the residual affinity of the three benzene nuclei (Thiele); little affinity is therefore left for the hydroxyl, which becomes ionisable (Walden). In the quinonoid form, the hydroxyl group would be attached to a carbon atom saturated by the great residual affinity of the atoms at the end of a chain of contiguous ethylenic linkings (compare pentadiene, Thiele), and therefore also weakly bound and ionisable. Hence it is evident that when such a compound is dissolved in an ionising solvent, the great mobility of the electric charge must cause an equilibrium in which ions of either form are present. The constant

$$k_1 = c_{\text{quinonoid ion}} / c_{\text{benzenoid ion}}$$

is determined mainly by the polarity of the atom linked to the positive corpuscle in either case, in the sense that the electron prefers the atom most strongly heteropolar or least isopolar to itself. Which of the two isomeric forms separates as a solid from such a solution depends on the product:

$$\frac{k_3 \times k_1}{k_2} \times \frac{\text{solubility of undissociated benzenoid form}}{\text{solubility of undissociated quinonoid form}} \quad \dots \quad (1).$$

If it is greater than 1, the quinonoid form separates, and vice versa. In this expression k_2 and k_3 are the dissociation constants

of the quinonoid and benzenoid forms respectively. These depend on the quantitative polar and steric factors, and their relative magnitude can therefore be ascertained by means of the present theory. It is seen that, whereas in the ion both forms are simultaneously present, the solid salt or hydroxy-compound may, *a priori*, correspond with either one of them.

When the quinonoid form of two compounds, I and II, gives a base of alkaline strength (oxonium, azonium, etc.), and therefore practically non-hydrolysed salts, it can be shown that the relative degree of hydrolysis of their benzenoid salts, with strong acids and for equivalent dilutions, very approximately corresponds with the equation:

$$\frac{c_{\text{hydrolysed I}}}{c_{\text{hydrolysed II}}} = \sqrt{\frac{k_{3\text{II}} \times k_{1\text{II}}}{k_{3\text{I}} \times k_{1\text{I}}}} \quad \dots \quad (2).$$

The tendency toward hydrolysis therefore is also a function of all the three factors, as the following few examples may demonstrate.

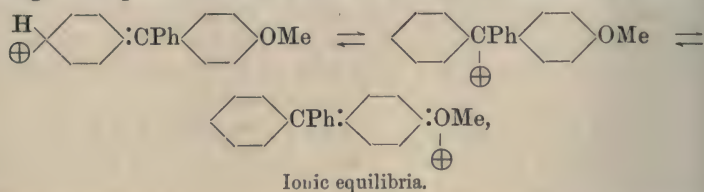
(a) *The Polar Factor*.—The dimethylamino-group is much more electropositive than methoxyl. In consequence, k_1 is much greater for *p*-dimethylamino-substituted triphenylcarbinols than for the corresponding methoxy-derivatives, and the former are hydrolysed to a much less extent than the latter. For the same reason, *N*-methylquinolinium salts are more stable than benzopyrilium salts. Since, for polar reasons, k_3 for a hydroxide or acetate, etc., is invariably much lower than for a chloride, sulphate, etc., whereas for the oxonium-, azonium-, etc., form, k_2 is of the alkaline order for the hydroxide as well as for all the salts, and since k_1 is independent of the anion, product (1) leads one to expect that the solid hydroxide, etc., will be benzenoid in many cases where the chloride, etc., are quinonoid.

(b) *The Quantitative Factor*.—An unsaturated substituent in the para-position raises the quantitative factor of k_3 , as shown by the formula:



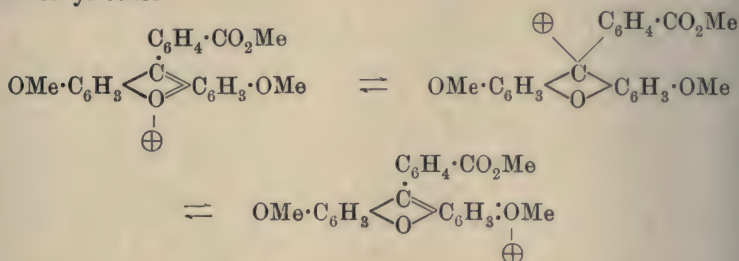
An independent proof for this is afforded by the fact that in such cases groups attached to the methane-carbon atom become labile and reactive even where ionisation and a quinonoid change are excluded. Thus phenylisoamylcarbinol can be distilled at 132° (Grignard, *Ann. Univ. Lyon*, 1901, No. 6, page 1), whereas its *p*-dimethylamino-derivative gives off water at 120° (Sachs and Weigert, *Ber.*, 1907, **40**, 4365), on account of the weakened linking of the hydroxyl group. When, accordingly, methoxyl is introduced into every para-position in triphenylcarbinol, each successive substitution

means, for the respective nucleus, a corresponding rise of k_3 , and, through the polar factor, also of k_1 . By equation (2), the suc-



cessive decrease of hydrolysis is therefore approximately geometrical (compare v. Baeyer and Villiger's "Potenzengesetz," *Ber.*, 1902, **35**, 3021). Similar considerations apply to the introduction of one, two, and three dimethylamino-groups in the para-positions of triphenylcarbinol (Hantzsch and Osswald, *Ber.*, 1900, **33**, 278), or of one and two of these groups in the para-position with respect to nitrogen in an azoxonium or azothionium salt (compare Kehrman, *Ber.*, 1906, **39**, 923).

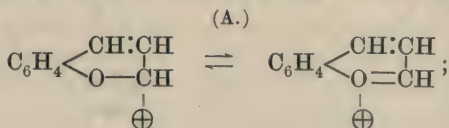
(c) *The Steric Factor.*—If the ionic equilibrium for fluorescein trimethyl ether:

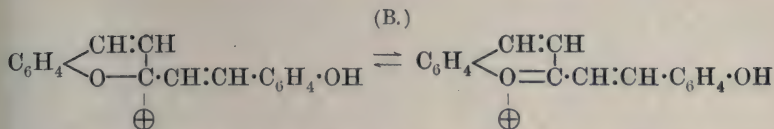


is compared with that for the similar compound not containing the carboxymethyl group, k_3 is nearly the same for both, since the steric and polar influence of the carboxyl group counterbalance each other. But k_1 , depending only on the polar factor, is much greater for the fluorescein, which is accordingly less hydrolysed, notwithstanding the presence of the additional negative substituent (Kehrman, *Ber.*, 1909, **42**, 870).

It is a disputed point whether these and similar ions (azoxonium, azothionium, etc.) are ortho- or para-quinonoid; it is seen that they are both. The relative preponderance of the competing equilibria depends on the respective products k_1 and k_2 .

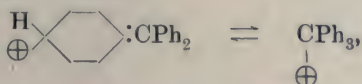
If the ionic equilibria for benzopyrylium salts are compared:





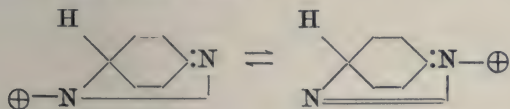
it is seen that for k_3 in B both the steric and quantitative factors are greater than in A; and the polar factor, and therefore k_1 , not being greatly different for A and B, B is hydrolysed to a less extent than A (Decker and Fellenberg, *Ber.*, 1907, **40**, 3818; Decker and Felser, *Ber.*, 1908, **41**, 3002).

In the ionic equilibrium,



an increase of the size of the anion raises the steric factor for k_3 ; accordingly, in these compounds the bromides are better conductors than the chlorides (Walden).

The above ionic equilibrium also facilitates the interpretation of the reactions of these compounds. If they were merely benzenoid in solution, the lability of para-substituting halogen atoms in dissociating solvents would be inexplicable; if a direct migration of the acidic radicle in the undissociated molecule were assumed to account for it (Gomberg), then triphenylmethyl chloride in sulphur dioxide would be transformed into *p*-chlorotriphenylmethane, since hydrogen is much more mobile than chlorine. According to the theory advanced in this paper, the exchange of halogen exclusively occurs in the quinonoid ion, and, the electric charge being much more mobile than hydrogen, the former only migrates to the central atom. It also follows from this that salts and double salts obtainable from a benzenoid carbinol or halogenide in a non-dissociating solvent must themselves be benzenoid, whatever their colour (compare v. Baeyer, Tschitschibabin). The same applies to the corresponding derivatives of distyryl ketone and similar compounds. These deductions apply to many other ionic equilibria, for instance: diazonium salts*:



* The reasons why Cain's formulæ have been adopted in this paper are, in addition to those adduced by Cain (*Trans.*, 1907, **91**, 1049, and recent discussion with Hantzsch), the following:

1. The fact that only the normal, but not the *iso*-derivative, can directly change to the diazonium form; this excludes stereoisomerism, and is explained by Cain's formula.

acridinium salts:



etc.

EXPERIMENTAL

In order to effect a quantitative estimation of the volatile amines obtained in the benzene layer by Farmer and Warth's distribution method, it is not feasible to precipitate the amine by hydrogen chloride and then to collect it. For, apart from partial thermic dissociation on drying, the mechanical losses preclude a sufficient accuracy, especially when it is remembered that the weight of the amine in the benzene layer, and therefore any experimental error in its determination, is multiplied by 20, after which the weight of the amine in the aqueous layer is obtained by subtraction.

(a) *Determination as Acetates.*—By adding a small excess of acetic anhydride to the benzene layer, and then distilling off the

2. The fact that only the *isodiazohydroxide*, but not the normal one, changes to a nitrosoamine excludes stereoisomerism, and is explained by Cain's formula.

3. The quantitative and polar factors being the same for *syn*- and *anti*-isomerides, but the steric factor being greater for the *syn*-, the latter would be the stronger acid. The reverse is, however, the case, notwithstanding the fact that the secondary change of the undissociated hydroxide, which would shift the electrolytic equilibrium in its favour, is generally more pronounced for the *iso*- than for the normal compound.

4. An objection against Cain's formulæ has now been removed by the recent discovery of azomethane, whereas no 'aliphatic' diazonium compound has yet been obtained.

5. The fact that diazonium salts do not show the characteristic reactions of the ethylenic bonds of a quinone is in perfect harmony with Cain's views; according to universal experience, especially as regards benzene substitution, trivalent nitrogen is more unsaturated than an ethylenic linking, so that bromine, for instance, is first added by trivalent nitrogen, whereby the quinonoid configuration disappears, and a perbromide of Chattaway's formulation is produced. Similarly, hydrogen is first added by trivalent nitrogen in the diazonium ion, and the bridge being thereby opened, only a hydrazine, but not a diamine, can result. Oxygen, also, is primarily added by the trivalent nitrogen of the diazonium ion, the bridge being broken, and a nitroamine produced.

6. Other formulæ that have been put forward seem to be highly improbable. There are steric objections against Euler's formula, whereas Morgan's seems an unnecessary complication. Cain's views leave room, of course, for an analogous ortho-quinonoid formula; but since Hantzsch (*Ber.*, 1903, **36**, 2069; Hantzsch and Smythe, *Ber.*, 1900, **33**, 505) has shown that the replacement of *o*- and *p*-substituents in the nucleus of diazo-compounds probably occurs in the *isodiazo*-form, it need not have any bearing on the constitution of the normal diazo- and diazonium compounds.

benzene and drying at 100° , the amine may be determined in a fairly exact way in some cases, whereas no constant weight is obtained in others. Thus, with *p*-bromoaniline, the weight of the acetyl derivative was invariably too low.

(b) *Determination as Hydrochlorides*.—The benzene was distilled off in a current of dry hydrogen chloride, and the residue, together with the flask (which had been weighed when dry), heated for an hour in a current of the same gas at 100° ; before opening the flask, the hydrogen chloride was expelled by dry carbon dioxide. At first a cork stopper was used, and two tests gave the following results:

p-Chloroaniline: 0.5774 gave 0.7394 hydrochloride; calculated, 0.7424; difference, $0.0030 = 0.4$ per cent.

p-Chloroaniline: 0.4822 gave 0.6179 hydrochloride; calculated, 0.6199; difference, $0.0020 = 0.32$ per cent.

Subsequently it was found that, after repeated use, traces of the cork dissolved in the benzene under the action of the acid, and a washing flask with ground-in stopper was therefore used.

(c) *Determination as Picrates*.—An experimentally simpler and, in view of reduced thermic dissociation, also better method consists in heating about 1 gram of picric acid to constant weight, at 100° , in a wide-necked 120 c.c. flask. The benzene solution is then introduced, the solvent distilled off, the flask heated for about forty-five minutes at 100° , and the weight of the amine obtained by subtraction. The flask is then heated for another hour, when the loss should be less than 0.0010 gram. If it is more, heating should be continued until it is less (per hour), and until the loss becomes constant (due to thermic dissociation only); this constant loss per hour, multiplied by the time of heating, must then be added to the final weight.

m-Bromoaniline: 0.0962 gave 0.0965 after heating for thirty minutes, and 0.0956 after seventy minutes.

p-Anisidine: 0.1166 gave 0.1169 after six hours; in this case prolonged heating was necessary, whereas nearly always forty-five minutes were sufficient, since, probably through traces of oxidation, the mass became coloured and tenaciously retained some benzene. As the anisidine picrate showed no thermic dissociation whatever, the weight became finally constant and was correct, notwithstanding the prolonged heating.

Since the picrate method gave results as accurate as could be desired, the results by that method are alone given in detail, those by the hydrochloride method being shortly mentioned for comparison. For *p*-anisidine, however (see Part III), the latter method was found to be preferable, there being no oxidation in that case.

Determination of Affinity Values.—In each case specially pure preparations were procured. The values were calculated by the formulæ given by Farmer and Warth (*loc. cit.*). The results by the picrate method do not vary by more than 5 per cent., a limit which has been declared by Ostwald to be admissible even for the direct conductivity method (*Zeitsch. physikal. Chem.*, 1889, **31**, 73). They differ by less than 10 per cent. from Bredig's conductivity values, which, in one case, differ by 18 per cent. from each other.

The letters again signify: F =distribution coefficient; c_1 =initial concentration of acid; c_2 =total initial concentration of amine; x =hydrolysis; v =dilution; s =substance used (in grams); r =substance obtained from benzene layer. Where salt is added under s , the hydrochloride of the amine was used; in the other cases, the free amine and the amount of N -hydrochloric acid corresponding with c_1 were employed.

m-Toluidine.—A specimen was prepared from *p*-toluidine by acetylation, nitration, hydrolysis, elimination of the amino-group, and reduction:

	<i>s.</i>	<i>r.</i>	<i>F.</i>			
	0·1623	0·0907	31·9			
	0·0763	0·0428	32·06		Average, 32.	
<i>s.</i>	<i>r.</i>	<i>c₂.</i>	<i>c₁.</i>	<i>v.</i>	<i>w.</i>	<i>k.</i>
0·9299 (salt)	0·0357	0·00648	0·00648	154·3	0·056	$5·48 \times 10^{-10}$

Specimen from Kahlbaum, which was redistilled:

2.1794 (salt)	0.0561	0.0152	0.0152	65.8	0.037	5.46×10^{-10}
1.8753 (salt)	0.0518	0.0131	0.0131	76.3	0.0397	5.49×10^{-10}
Average, 5.48×10^{-10} .						

By Hydrochloride Method:

$$s=1.59; v=67; x=0.0353; k=6.10 \times 10^{-10}.$$

p-Toluidine (Kahlbaum):

	<i>s.</i>	<i>r.</i>	<i>F.</i>			
	0.0952	0.0528	31.0			
	<i>s.</i>	<i>r.</i>	<i>c₂.</i>	<i>c₁.</i>	<i>v.</i>	<i>x.</i>
	2.6247	0.0376	0.0183	0.0183	54.6	0.0207
(salt)						1.48 × 10 ⁻⁹

m-Chloroaniline (Schuchardt):

<i>s.</i>	<i>r.</i>	<i>F.</i>				
0·3316	0·2370	83·6	Average, 85·2.			
0·3169	0·2279	86·8				
<i>s.</i>	<i>r.</i>	<i>c₂</i>	<i>c₁</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0·7793	0·2423	0·00613	0·00613	163	0·21	$3·45 \times 10^{-11}$
0·7984	0·2465	0·00626	0·00626	160	0·208	$3·45 \times 10^{-11}$
				Average, $3·45 \times 10^{-11}$.		

By Hydrochloride Method:

$$s=1.8143; v=70.4; x=0.142; k=3.56 \times 10^{-11}.$$

m-Bromoaniline (Schuchardt):

<i>s.</i>	<i>r.</i>	<i>F.</i>				
0.1916	0.1493	162.3				
0.3156	0.2449	155.5				
			Average, 158.9			
<i>s.</i>	<i>r.</i>	<i>c₂.</i>	<i>c₁.</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.2988	0.1673	0.00174	0.00175	575	0.345	3.73×10^{-11}
0.3397	0.1571	0.00163	0.00163	613.5	0.347	3.92×10^{-11}
(salt)						Average, 3.82×10^{-11} .

By Hydrochloride Method:

$$s=0.3180; v=540.5; x=0.351; k=3.36 \times 10^{-11}.$$

p-Chloroaniline (Schuchardt):

<i>s.</i>	<i>r.</i>	<i>F.</i>				
0.2177	0.1478	64.0				
0.2030	0.1379	64.1				
			Average, 64			
<i>s.</i>	<i>r.</i>	<i>c₂.</i>	<i>c₁.</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.8173	0.1222	0.00498	0.00498	201	0.143	9.9×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=1.9702; v=64.73; x=0.084; k=9.9 \times 10^{-11}.$$

p-Bromoaniline (Kahlbaum):

<i>s.</i>	<i>r.</i>	<i>F.</i>				
0.1929	0.1447	115.8				
0.1908	0.1428	113.8				
			Average, 114.8.			
<i>s.</i>	<i>r.</i>	<i>c₂.</i>	<i>c₁.</i>	<i>v.</i>	<i>x.</i>	<i>k.</i>
0.3443	0.1141	0.00165	0.00165	606	0.248	8.8×10^{-11}
(salt)						

By Hydrochloride Method:

$$s=2.0975; v=82.0; x=0.0975; k=9.2 \times 10^{-11}.$$

It will be noticed that by the picrate method, dilutions varying from 54.6 to 613.5 could be employed, whereas Farmer and Warth's dilutions were much smaller, varying from 10.0 to 64.1.

The author is again indebted to Dr. Senter for kind criticism.

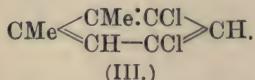
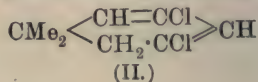
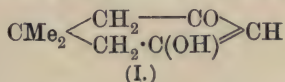
FLEET, HANTS.

XI.—3:5-Dichloro-o-phthalic Acid.

By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN.

IN a recent number of the *Berichte* (1909, 42, 3529), Villiger described the preparation of three of the four possible dichloro-o-phthalic acids (Cl:Cl, 3:6, 3:4, 4:5) by the direct chlorination of phthalic anhydride. Villiger points out (*ibid.*, p. 3532) that a fourth isomeride was described by Crossley and Le Sueur in 1902 (*Trans.*, 81, 1533), and regards the acid as 3:5-dichloro-o-phthalic acid, although "its constitution has never been controlled."

The acid described by Crossley and Le Sueur was prepared by the direct oxidation with dilute nitric acid of a substance believed to be 3:5-dichloro-o-xylene. This chloro-derivative (III) was obtained as a by-product in the action of phosphorus pentachloride on



dimethyldihydroresorcin (I) [the main product being 3:5-dichloro-1:1-dimethylcyclohexadiene (II)], and this structure was assigned to it because there did not appear to be any reason to presume that, in the conversion of the hydroaromatic into the aromatic dichloro-derivative, the chlorine atoms would alter their positions. During the reaction, however, a methyl group must have wandered, and this was shown to have migrated to the ortho-position, because on oxidation an acid was obtained which readily gave an anhydride, and also the fluorescein reaction. Villiger is right in saying that, at that time (1902), the constitution of the dichloro-acid had not been controlled either by an analytical or a synthetical method, but this check on the constitution has since been recorded.

In 1904 (*Trans.*, 85, 284) Crossley showed that the dichloro-o-xylene, obtained from dimethyldihydroresorcin, gave, on treatment with a nitrating mixture, a dichlorodinitro-o-xylene melting at 175—176°, and in 1909 (*Trans.*, 95, 205) Crossley and Renouf showed that this same dichlorodinitro-o-xylene could be obtained from 3:5-(or 4:6-)dinitro-o-xylene by reducing the two nitro-groups to amino-groups, replacing the latter by chlorine atoms, and nitrating the dichloro-o-xylene so obtained. This series of reactions obviously proved that the dichloroxylylene obtained from dimethyldihydroresorcin is identical with that prepared by replacing the nitro-groups in 3:5-dinitro-o-xylene by chlorine atoms, and hence it must be

3:5-dichloro-*o*-xylene. The properties of the two specimens of dichloro-*o*-xylene were not, however, carefully compared, nor was the dichloroxylene, obtained from 3:5-dinitro-*o*-xylene, oxidised to the corresponding phthalic acid, but this has now been completed under similar conditions to those previously described, and the results are given in the following table:

	From dimethyl- dihydroresorcin.	From 3:5-di- nitro- <i>o</i> -xylene.
Dichloroxylene	Yellow, refractive liquid ; slight aromatic odour. B. p. 226°, m. p. 3—4°.	Yellow, refractive liquid ; slight aromatic odour. B. p. 226°, m. p. 5—7°.
Dichlorodinitroxylene	M. p. 175—176°.	M. p. 176°.
Dichlorophthalic acid	M. p. 164° (previous soft- ening) with evolution of gas.	M. p. 164° (previous soft- ening) with evolution of gas.
Dichlorophthalic anhydride	M. p. 89°.	M. p. 89°.
Dichlorophthalanil	M. p. 150—150·5°.	M. p. 150°.

In all cases the above melting points of the two corresponding series of substances were checked by the mixed melting-point method.

This direct synthesis of 3:5-dichloro-*o*-phthalic acid proves beyond doubt the correctness of the conclusions as to the constitution of the acid obtained by Crossley and Le Sueur from dimethyldihydroresorcin.

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XII.—*The Constituents of Colocynth.*

By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

UNDER the title of "Colocynth" the various national Pharmacopœias recognise the dried, peeled fruit, or the dried pulp of the fruit, of *Citrullus Colocynthis*, Schrader. Although this fruit has been used medicinally for a very long period, and has been the subject of several investigations, no complete chemical examination has hitherto been made of it, and the various products described in the literature as having been obtained therefrom were either amorphous or of an indefinite nature. It was recorded, for example, many years ago by Walz (*N. Jahrb. Pharm.*, 1858, 9, 16, 225; 1861, 16, 10) that colocynth contains a bitter glucoside, designated "colocynthin," which, although usually forming a yellow, amorphous mass, could be obtained in a crystalline state by the slow evaporation of its alcoholic solution.

This so-called colocynthin, to which the formula $C_{56}H_{84}O_{23}$ was assigned, was stated to yield, on heating with dilute acids, dextrose and "colocynthein," the latter having been described as an amorphous resin. The same investigator noted the occurrence of a tasteless, crystalline substance, designated "colocynthitin," which was found to be insoluble in water and cold absolute alcohol, but soluble in boiling alcohol and ether, although its characters do not appear to have been further determined. Henke (*Arch. Pharm.*, 1883, **221**, 200) could obtain a product corresponding with colocynthin only in the form of a yellow, amorphous powder, and was unable to confirm the statement respecting its glucosidic character. Johannson (*Zeitsch. anal. Chem.*, 1885, **24**, 154) has stated that "colocynthin, when heated with dilute sulphuric acid, yields colocynthein, elaterin, and bryonin," and he recorded some colour reactions which were supposed to differentiate these products.

Naylor and Chappel (*Pharm. J.*, 1907, [iv], **25**, 117), in a paper entitled: "On *Cucumis trigonus*, Roxb., and Colocynthin," have compared a product obtained by them from the fruit of the above-mentioned species of *Cucumis*, indigenous to India, with the so-called "colocynthin" obtained from colocynth by Henke's method and by a modification of the latter. It is stated that whilst the product obtained from either the Indian fruit or from colocynth by Henke's process was amorphous, "that resulting from the modified process was most largely deposited on spontaneous evaporation of its solvent in pale yellow needles." They were thus led to conclude, in the first place, that "colocynthin prepared from *Citrullus Colocynthis* may be obtained in a crystalline state, despite the failure of Henke and of Wagner to induce it to assume a crystalline form"; secondly, that notwithstanding the doubts cast by Henke upon its decomposition by acids into colocynthein and a sugar, their results on the contrary confirm those of Johannson (*loc. cit.*), that colocynthin is capable of hydrolysis, and that it yields, amongst other products, colocynthein and elaterin, to which they may add—and a sugar, dextrose. The same authors furthermore state that "colocynth contains a white, crystalline body, agreeing in its general characters with the colocynthetin (*colocynthitin*) of Walz." There is, however, no evidence that any of the products prepared and examined by Naylor and Chappel were pure or homogeneous substances, and their comparison of them was chiefly restricted to certain colour reactions which are by no means characteristic of the substances they are supposed to identify. On the other hand, it may quite safely be assumed that the products referred to were very indefinite mixtures.

The present investigation has shown that colocynth contains a considerable amount of α -elaterin (*Trans.*, 1909, **95**, 1989), which

is present in the free state, together with other compounds which have not previously been isolated. A complete summary of the results now obtained, with the deductions from them, is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation was Turkish colocynth, consisting of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader. The original weight of this material was 105 kilograms. After separating as completely as possible the seeds from the pulp, the latter was found to weigh 25.6 kilograms, or 24.4 per cent. of the whole. The seeds amounted to 79.3 kilograms, thus representing 75.5 per cent. of the weight of the entire peeled fruit.

A small portion (10 grams) of the above-mentioned pulp was subjected to the test for an alkaloid, when reactions were obtained indicating the presence of an appreciable amount of such a substance.

A further portion (20 grams) of the ground pulp was extracted successively in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained.

Petroleum (b. p. 35—50°) extracted	0.33 gram	=	1.65 per cent.
Ether	1.75 "	=	8.75 "
Chloroform	1.06 "	=	5.30 "
Ethyl acetate	0.61 "	=	3.05 "
Alcohol	0.92 "	=	4.60 "

Total 4.67 grams = 23.35 per cent.

For the purpose of a complete examination, 24.6 kilograms of [the ground colocynth pulp were completely extracted with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark-coloured extract was obtained, amounting to 6.63 kilograms.

Distillation of the Extract with Steam.

A quantity (2 kilograms) of the above-mentioned extract, representing 7.42 kilograms of the pulp, was mixed with water, and steam passed through the mixture for several hours. The distillate, which amounted to 4 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when a small quantity of an essential oil was obtained. This was a pale yellow liquid, which possessed a characteristic odour, and, after some time, deposited a small amount of a crystalline substance. The amount of this oil was, however, too small to permit of its further investigation.

Non-volatile Constituents of the Extract.

After the distillation of the extract with steam, as described above, there remained in the distillation flask a dark-coloured, aqueous liquid (A) and a quantity of a brown resin (B). The latter was collected and repeatedly washed with water until nothing further was removed, the washings being added to the above-mentioned aqueous liquid.

*Examination of the Aqueous Liquid (A).**Isolation of a New Dihydric Alcohol, Citrullol, $C_{22}H_{36}O_2(OH)_2$.*

The aqueous liquid (A), which amounted to 6.5 litres, was repeatedly extracted with ether, and the ethereal extracts united, after which a quantity of a colourless, sparingly soluble substance which accompanied them was separated by filtration.

This substance was almost insoluble in all the ordinary solvents, and appears to have been contained in the aqueous liquid in a colloidal form. It was, however, readily soluble in hot pyridine, from which it crystallised in glistening plates, melting and decomposing at 285—290°. The quantity so obtained was 0.9 gram:

0.1253 gave 0.3310 CO_2 and 0.1192 H_2O . $C = 72.0$; $H = 10.6$.

$C_{22}H_{38}O_4$ requires $C = 72.1$; $H = 10.4$ per cent.

This substance, when dissolved in chloroform with a little acetic anhydride, gave on the addition of a few drops of concentrated sulphuric acid a series of colour reactions similar to those produced by ipuranol, $C_{28}H_{38}O_2(OH)_2$ (Trans., 1909, 95, 249), and it appears, in fact, to be a lower homologue of the latter. As it does not agree in its properties with any substance of the above formula which has hitherto been described, it is proposed to designate it *citrullol*, with reference to the generic name of the plant from which it has been obtained.

It was ascertained that citrullol exhibits no physiological activity when administered to a dog in doses of 0.05 gram.

Diacetylcitrullol, $C_{22}H_{36}O_4(CO \cdot CH_3)_2$.—This was obtained by heating citrullol with acetic anhydride, from which it separated in glistening needles, melting at 167°:

0.1330 gave 0.3378 CO_2 and 0.1098 H_2O . $C = 69.3$; $H = 9.2$.

$C_{26}H_{42}O_6$ requires $C = 69.3$; $H = 9.3$ per cent.

The ethereal liquid from which the citrullol had been separated by filtration, as above described, was subsequently evaporated, but it yielded only a resinous product from which nothing definite could be isolated.

Isolation of an Alkaloidal Principle.

The aqueous liquid, which had previously been extracted with ether, was treated with a solution of basic lead acetate. This produced a voluminous, yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture a liquid was obtained which, after acidifying with hydrochloric acid, responded to the ordinary alkaloid reagents. It was rendered alkaline by means of ammonia, and extracted many times with chloroform. The chloroform extracts were united and repeatedly shaken with dilute (10 per cent.) hydrochloric acid. The acid liquids were at once brought into a solution of ammonia, and the precipitated base extracted by means of chloroform. On the evaporation of the solvent there was obtained a small amount (about 5 grams) of a light brown product, which was resinous in character, very weakly basic, and possessed an extremely bitter taste. It dissolved sparingly in dilute acids, and was precipitated from its solutions by the usual alkaloid reagents, including tannin. Neither the free base nor its salts could be obtained in a crystalline condition. On warming the base with alkali hydroxides it dissolved, and, on prolonged boiling, ammonia was evolved. When heated with 20 per cent. hydrochloric acid it yielded ammonia and pyridine, the latter having been identified by its odour, and by the formation of its platinochloride.

The basic principle was not glucosidic, as no sugar was formed on boiling its acid solutions. It represents one of the physiologically active constituents of colocynth, as doses of 0.1 gram administered to dogs produced very drastic purgation.

The filtrate from the above-mentioned basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a small volume. It was then treated with a large volume of strong alcohol, which effected the precipitation of a quantity of inorganic salts, consisting chiefly of the chloride, sulphate, and nitrate of potassium, together with a little sugar. The latter yielded *d*-phenylglucosazone, melting at 208—210°. The clear alcoholic liquid was decanted from the precipitated material, mixed with purified sawdust, and the thoroughly dried mixture extracted in a Soxhlet apparatus with chloroform. This removed a small quantity of a brown syrup, which, on hydrolysis, yielded a sugar which readily reduced Fehling's solution, and from which *d*-phenylglucosazone, melting at 208—210°, was prepared. It is therefore evident that the aqueous liquid contained a very small amount of a glucosidic substance, but this could

not be obtained in a form which would permit of its being more definitely characterised.

Examination of the Resin (B).

Isolation of α -Elaterin.

This resin was a brown solid, which softened below 100° , and amounted to 675 grams. It was digested with about 2 litres of strong alcohol, in which it only partly dissolved. The undissolved portion was collected, washed first with alcohol, and then with ether, when it was obtained in small, colourless crystals, melting and decomposing at $227-230^{\circ}$. On recrystallising this product from alcohol, it formed small, glistening, hexagonal prisms, melting and decomposing at 232° . The amount of crystalline substance thus obtained was 80 grams, corresponding with about 1.08 per cent. of the weight of colocynth pulp employed:

0.1446 gave 0.3655 CO_2 and 0.1060 H_2O . $\text{C} = 68.9$; $\text{H} = 8.1$.

$\text{C}_{20}\text{H}_{28}\text{O}_5$ requires $\text{C} = 68.9$; $\text{H} = 8.0$ per cent.

$\text{C}_{24}\text{H}_{34}\text{O}_6$ " $\text{C} = 68.9$; $\text{H} = 8.0$ " "

$\text{C}_{28}\text{H}_{38}\text{O}_7$ " $\text{C} = 69.1$; $\text{H} = 7.8$ " "

This substance agrees in crystalline form, melting point, and solubility, and in all its chemical properties with α -elaterin, as previously described by us (Trans., 1909, 95, 1989). Its empirical formula cannot yet be considered definitely established.

A determination of its specific rotatory power gave the following result:

0.3121, made up to 20 c.c. with chloroform, gave $\alpha_D - 2^{\circ}9'$ in a 2-dem. tube, whence $[\alpha]_D - 68.9^{\circ}$.

The alcoholic solution of the resin (B), from which the α -elaterin had been separated by filtration as above described, together with the alcoholic and ethereal washings from the latter, was mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with light petroleum (b. p. $35-50^{\circ}$), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin (B).

Isolation of Hentriacontane, $\text{C}_{31}\text{H}_{64}$, and a Phytosterol, $\text{C}_{27}\text{H}_{46}\text{O}$.

This extract was a dark green, waxy solid, and amounted to 34 grams. It was dissolved in ether, the ethereal solution being successively shaken with dilute aqueous sodium carbonate and sodium hydroxide, which, however, removed nothing. The ether was accordingly evaporated, and the residue hydrolysed by boiling with an

alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a crystalline product was obtained. This was dissolved in 250 c.c. of absolute alcohol, and the solution kept for some hours, when a small quantity of an almost colourless substance separated. This was collected and washed with cold alcohol, after which it was distilled under diminished pressure. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when small, glistening, colourless leaflets, melting at 68° , were obtained :

0.1344 gave 0.4176 CO_2 and $0.1824 \text{ H}_2\text{O}$. $\text{C} = 84.7$; $\text{H} = 15.0$.

$\text{C}_{31}\text{H}_{64}$ requires $\text{C} = 85.3$; $\text{H} = 14.7$ per cent.

The substance was thus identified as hentriacontane.

The alcoholic solution from which the hentriacontane had been removed by filtration was concentrated to a small volume and diluted with water, when a quantity of a crystalline substance separated. This was collected and washed with a little ethyl acetate, after which it was distilled under diminished pressure. The distillate was crystallised from a mixture of dilute alcohol and ethyl acetate, when it formed colourless, glistening leaflets, melting at $160\text{--}162^{\circ}$. The amount of substance so obtained was 1.3 grams :

0.2205, heated at 115° , lost $0.0104 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 4.7$.

0.1493 gave 0.4560 CO_2 and $0.1590 \text{ H}_2\text{O}$. $\text{C} = 83.3$; $\text{H} = 11.8$.

$\text{C}_{27}\text{H}_{46}\text{O}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.5$ per cent.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C} = 83.9$; $\text{H} = 11.9$ per cent.

This substance thus agrees in composition with a phytosterol, and it yielded the colour reactions of this class of compounds. It was found to be optically inactive, and in this respect appears to differ from any of the phytosterols which have hitherto been recorded. The acetyl derivative, when crystallised from acetic anhydride, separated in glistening plates, melting at $175\text{--}177^{\circ}$.

Examination of the Fatty Acids.

The aqueous, alkaline solution of potassium salts, from which the hentriacontane and phytosterol had been removed by extraction with ether, was acidified and again extracted with ether. The ethereal solution was washed, dried, and the solvent removed, when a quantity (12 grams) of fatty acids was obtained which, when distilled under diminished pressure, passed over between 220° and $250^{\circ}/15 \text{ mm}$. Ten grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when the greater portion dissolved. Both the soluble and insoluble portions were decomposed by hydro-

chloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 8 grams of liquid acids, whilst the insoluble portion gave 1.5 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 225° and $235^{\circ}/15$ mm. An analysis and a determination of the iodine value gave the following results:

0.1406 gave 0.3964 CO_2 and 0.1460 H_2O . $\text{C} = 76.9$; $\text{H} = 11.5$.

0.5625 absorbed 0.8346 iodine. Iodine value = 148.4.

$\text{C}_{18}\text{H}_{34}\text{O}_2$ requires $\text{C} = 76.6$; $\text{H} = 12.1$ per cent. Iodine value = 90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ „ $\text{C} = 77.1$; $\text{H} = 11.4$ „ „ Iodine value = 181.4.

In order to obtain more definite information respecting the nature of the above mixture, a quantity of it was oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I., p. 360). This resulted in the formation of dihydroxystearic acid (m. p. $125-127^{\circ}$) and tetrahydroxystearic acid (m. p. $157-160^{\circ}$), the latter in predominating amount.

It may thus be concluded that the liquid acids consisted chiefly of a mixture of oleic and linolic acids, the latter predominating.

The Solid Acids.—These acids melted at $56-58^{\circ}$, and, on analysis, gave the following result:

0.1430 gave 0.3955 CO_2 and 0.1636 H_2O . $\text{C} = 75.4$; $\text{H} = 12.7$.

$\text{C}_{16}\text{H}_{32}\text{O}_2$ requires $\text{C} = 75.0$; $\text{H} = 12.5$ per cent.

$\text{C}_{18}\text{H}_{36}\text{O}_2$ „ $\text{C} = 76.1$; $\text{H} = 12.7$ „ „

By repeated crystallisation from acetic acid a small amount of an acid melting at $68-69^{\circ}$ was obtained, from which a silver salt was prepared and analysed:

0.2118 gave 0.0576 Ag. $\text{Ag} = 27.2$.

$\text{C}_{18}\text{H}_{35}\text{O}_2\text{Ag}$ requires $\text{Ag} = 27.6$ per cent.

From the above results it is evident that the solid acids consisted of a mixture of palmitic and stearic acids.

Ether and Chloroform Extracts of the Resin (B).

These extracts amounted to 169 and 180 grams respectively. They were light-coloured resins, and, with the exception of about 10 grams of α -elaterin and a little of the previously-mentioned citrullol, nothing definite could be isolated from them. When heated with a solution of sulphuric acid in dilute alcohol they yielded no sugar, and therefore contained nothing glucosidic.

Both of the above-mentioned extracts were found to possess a very marked cathartic action, which was doubtless due in part to

the presence of small quantities of the previously described alkaloidal principle, as about 3 grams of the latter were obtained from them. The activity of the extracts was, however, not appreciably diminished by the complete removal of the alkaloidal principle, as they then produced drastic purgation when administered to dogs in doses of 0.1 gram.

Ethyl Acetate and Alcohol Extracts of the Resin (B).

These extracts were brown resins, amounting to 85 and 100 grams respectively, and nothing definite could be isolated from them. They were not glucosidic, and possessed no purgative action.

Examination of Colocynth Seeds.

The material required for the proceeding investigation of the pulp of colocynth fruit having rendered available a large quantity of the seeds, it appeared desirable to examine the latter with respect to their more important constituents.

A small portion (10 grams) of the crushed seed was tested for the presence of an alkaloid by treatment with Prollius's fluid, when distinct reactions were obtained with the usual reagents. These reactions were probably due to the presence of a very small amount of the same alkaloidal principle as that contained in the pulp of the fruit.

Separation of an Enzyme.

A quantity (2 kilograms) of the crushed seed was extracted by percolation with cold light petroleum for the removal of the fatty oil, after which the material was mixed with cold water and the mixture kept for several hours. The aqueous liquid was then expressed and filtered, and to it a quantity of strong alcohol was added. A voluminous, light-coloured precipitate was thus produced, which was collected, washed with a little alcohol, and dried in a desiccator. The product so obtained amounted to 10 grams, and, although containing a large proportion of inorganic material, it readily hydrolysed β -glucosides.

The Fatty Oil.

The amount of fatty oil contained in the seed, as determined by the extraction of 50 grams of the ground material in a Soxhlet apparatus with light petroleum (b. p. 35—50°), was 12.72 per cent.

The oil obtained was a clear pale yellow liquid, which was devoid of optical activity. A determination of its constants gave the following results: specific gravity, 20°/20° = 0.9273; acid value, 2.6; saponification value, 186.7; iodine value, 126.6.

Hydrolysis of the Fatty Oil. Isolation of a Phytosterol, $C_{20}H_{34}O$.

A quantity (150 grams) of the oil was hydrolysed by boiling with alcoholic potassium hydroxide, the alcohol removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and the solvent removed, when a small quantity of a crystalline substance was obtained. This was distilled under diminished pressure, after which it was crystallised from a mixture of dilute alcohol and ethyl acetate, when it separated in colourless, glistening plates, melting at $158-160^{\circ}$. The amount of substance so obtained was 0.3 gram:

0.1700 gave 0.5154 CO_2 and 0.1724 H_2O . $C = 82.7$; $H = 11.3$.

$C_{20}H_{34}O$ requires $C = 82.8$; $H = 11.7$ per cent.

This substance was evidently a phytosterol, and it yielded the colour reactions of this class of compounds. A determination of its specific rotatory power gave the following result:

0.2473, made up to 20 c.c. with chloroform, gave $\alpha_D + 0^{\circ}12'$ in a 2-dcm. tube, whence $[\alpha]_D + 8.1^{\circ}$.

The acetyl derivative, when crystallised from acetic anhydride, separated in glistening plates, melting at $167-170^{\circ}$.

The Fatty Acids.

The alkaline solution of potassium salts, which had been extracted with ether as above described, was acidified and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. The fatty acids thus obtained amounted to 87 per cent. of the weight of the oil. When distilled under diminished pressure, they passed over between 240° and $245^{\circ}/15$ mm. as a viscous liquid, which solidified on cooling to a soft, nearly colourless mass. A determination of the constants of the total acids gave the following results:

Melting point (complete fusion), $29.5-32^{\circ}$; specific gravity, $50^{\circ}/50^{\circ} = 0.8910$; neutralisation value, 195.6; iodine value 131.1.

These constants, both for the fatty oil and the total acids obtained therefrom, are in fairly close agreement with those recently recorded by Grimaldi and Prussia (*Chem. Zeit.*, 1909, **33**, 1239). The last-mentioned investigators had, however, extracted the colocynth seeds by means of carbon tetrachloride, and describe the oil as having a reddish-yellow colour with a slight green fluorescence.

Summary.

The results of the preceding investigation may be summarised as follows:

The material employed consisted of the dried, peeled fruit of *Citrullus Colocynthis*, Schrader. The pulp of the fruit, deprived of its seeds, represented 24.4 per cent. of the whole.

On extracting the pulp with alcohol, and subjecting the resulting extract to distillation with steam, a very small amount of a pale yellow essential oil was obtained. From the portion of the extract which was soluble in water, the following substances were isolated: (i) A new dihydric alcohol, $C_{22}H_{36}O_2(OH)_2$ (m. p. 285—290°), designated as *citrullol*, which is apparently a lower homologue of ipuranol, and yields a *diacetyl* derivative melting at 167°. (ii) An amorphous, alkaloidal principle, which is a very weak base, and from which no crystalline derivative could be prepared; it possesses an extremely bitter taste, and represents one of the purgative principles of the fruit. The aqueous liquid from which the above-mentioned substances were isolated contained, furthermore, a quantity of inorganic salts, a little sugar, and a very small amount of an amorphous, glucosidic substance.

The portion of the alcoholic extract which was insoluble in water consisted chiefly of resinous material, from which, however, a quantity of α -elaterin (m. p. 232°; $[\alpha]_D - 68.9^\circ$) was isolated (compare Trans., 1909, 95, 1989). After the separation of the latter substance, the resin was extracted with various solvents, when it yielded a small amount of hentriacontane, $C_{31}H_{64}$ (m. p. 68°); a phytosterol, $C_{27}H_{46}O$ (m. p. 160—162°, optically inactive); a mixture of fatty acids, and a further quantity of α -elaterin, together with a little of the above-described alkaloidal principle. None of the extracts from the resin were glucosidic. The ether and chloroform extracts possessed marked purgative properties, even after the complete removal of the active alkaloidal principle.

The seeds of the colocynth, which represented 75.5 per cent. of the entire peeled fruit, were found to contain traces of an alkaloidal principle, a small amount of an enzyme which hydrolyses β -glucosides, and a quantity of fatty oil corresponding to 12.72 per cent. of the weight of the seed. The constants of the fatty oil, and of the total fatty acids obtained therefrom, were determined, and from the oil a small amount of a phytosterol, $C_{20}H_{34}O$, was isolated, which melted at 158—160°, and had $[\alpha]_D + 8.1^\circ$.

The results of the present research have established the fact that the so-called "colocynthin" and "colocynthitin," as well as the other products obtained from colocynth by previous investigators to which specific names have been attached, consisted of mixtures of a very indefinite character, and that the amount of glucosidic substance contained in the fruit is extremely small. On the other hand, it has now been ascertained that the purgative action of colocynth is due to

at least two principles, one of which is alkaloidal, although a very weak base, and apparently incapable of forming any crystalline salts, whilst the other source of activity is represented by some non-basic principle or principles contained in both the ether and chloroform extracts of the resin. All the attempts to obtain the last-mentioned active principle in a more definite form were, however, unsuccessful. No evidence could be obtained of the presence in colocynth of β -elaterin, which constitutes the physiologically active constituent of the fruit of *Ecballium Elaterium*.

In conclusion, the authors desire to express their best thanks to Dr. H. H. Dale, Director of the Wellcome Physiological Research Laboratories, for having kindly conducted the numerous physiological tests involved in this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XIII.—*A Contribution to the Study of the Oxydases.*

By ROSS AIKEN GORTNER, Ph.D.

IN 1883 Yoshida (Trans., 1883, **43**, 472) discovered laccase, the first of the oxydases to be studied. Later Bertrand (*Compt. rend.*, 1896, **122**, 1215) found that another variety of this class was present in various examples of the vegetable world, for example, potatoes, bulbs of the dahlia, various mushrooms, such as *Russula nigricans*, etc. This oxydase differed radically from laccase in that it lost its vitality at 65—70°, and was also able to oxidise aqueous solutions of tyrosine through various colour stages (from pink to rose, violet, and blue-black), ending by a deposition of a black, melanin-like substance, and leaving the supernatant liquid completely decolorised. On account of this power of oxidising tyrosine, Bertrand gave the name tyrosinase to the oxydase.

Many authors* have since that time reviewed and extended the

* Biedermann (*Pflüger's Archiv*, 1898, **72**, 152); Biedermann and Moritz (*ibid.*, 1899, **75**, 43); Gessard (*Ann. Inst. Pasteur*, 1901, **15**, 593; *Compt. rend.*, 1903, **136**, 631; 1903, **138**, 774; *Compt. rend. Soc. Biol.*, 1902, **54**, 1304, 1398); v. Fürth and Schneider (*Beitr. Chem. Physiol. Path.*, 1901, **1**, 229); Durham (*Proc. Roy. Soc.*, 1904, **74**, 310); Wilcock (*J. Physiol.*, 1906, **34**, 207); Bonduoy (*Trav. Sci. Univ. Rennes*, 1903, **2**, 281; 1905, **4**, 67); Gautier (*ibid.*, 1905, **4**, 287); Weindl (*Arch. Ent'mech.*, 1907, **23**, 632); Bertrand and Rosenblatt (*Compt. rend.*, 1908, **146**, 304); Abderhalden and Guggenheim (*Zeitsch. physiol. Chem.*, 1908, **54**, 337); Wolff (*Compt. rend.*, 1909, **148**, 500; **149**, 467); Bach (*Ber.*, 1909, **42**, 594; *Biochem. Centr.*, 1909, **9**, 1, 73); Rocques (*Compt. rend.*, 1909, **149**, 418).

original work, so much so that tyrosinases have been found to be very widely distributed in nature, and to occur not only in many plants, but also in numerous animal bodies.

By far the greater portion of the European work has been done with the glycerol extracts of *Russula nigricans* (Bertrand, *loc. cit.*), *Russula queletii* (Bertrand and Rosenblatt, *loc. cit.*), *Russula delica* (Wolff, *Compt. rend.*, 1909, **148**, 500), *Russula noircissant* (Bertrand, *Ann. Inst. Pasteur*, 1908, **22**, 381), etc., but the occurrence of tyrosinase has been demonstrated in the ink sac of the squid (Przibram, cited by v. Fürth, *Vergleichende chemische Physiologie der niederen Tiere*, Jena, 1903, p. 372; Gessard, *Compt. rend.*, 1903, **136**, 631), in the hameolymph of various insects (v. Fürth and Schneider, *loc. cit.*), in wheat bran (Bertrand and Mutermilch, *Ann. Inst. Pasteur*, 1907, **21**, 833), in the intestinal fluid of meal worms (*Tenebrio molitor*) (Biedermann, *loc. cit.*), in molluscs (Biedermann and Moritz, *loc. cit.*), in gum arabic and mistletoe (Bonduoy, *loc. cit.*), and in plants which blacken during the process of drying (Gautier, *loc. cit.*), etc., etc.

Miss Durham (*loc. cit.*) states that she obtained evidence of the presence of tyrosinase in the skins of foetal and newly-born guinea pigs and rabbits of black or agouti origin. Inasmuch as her results depended on the addition of a milligram of ferrous sulphate as an "activator" (no darkening occurring in a tube containing "juices" and tyrosine but no ferrous sulphate), and, as will be shown later in this paper, a milligram of ferrous sulphate inhibits coloration almost completely—also since her "tyrosinase" (obtained from red guinea pigs) is the only known example of a tyrosine oxidising ferment which oxidises only to the orange stage (all others progressing to black), and lastly, since the pigment-like substances described in her work "are readily soluble in alkalis," unlike those produced by v. Fürth and Schneider (*loc. cit.*), and also by the author from the interaction of tyrosine and tyrosinase, these substances being found to be insoluble even in hot dilute sodium hydroxide or ammonia, it is apparent that her "tyrosinase" reaction, if not due to some section of the ferrous sulphate, is certainly due to an agent altogether distinct from that named by Bertrand "tyrosinase." The author has made several attempts to confirm her results, but has as yet obtained no trace of coloration induced by an oxydase.

In all the literature cited, the tyrosinase was that obtained by extracting with either glycerol or chloroform-water. Gessard (*Ann. Inst. Pasteur*, 1901, **15**, 601) states that the extract may be made with either chloroform-water or glycerol, but that the glycerol extract keeps best, and has no effect on the results.

The source of the tyrosinase in the experiments described in this paper varied somewhat, but the major portion of the work is devoted to the description of a new variety of this ferment, which is distinguished by absolute insolubility in water, the activity of which is destroyed by glycerol, by alcohol and ether, or by drying at room temperature; further, it does not oxidise resorcinol, orcinol (Wolff, *loc. cit.*), pyramidone (Bonduoy, *loc. cit.*), or quinol, thus in most of these reactions differing radically from the known tyrosinases.

EXPERIMENTAL.

Tyrosinase in the Intestinal Fluid of the Meal Worm (Tenebrio molitor).

Biedermann (*loc. cit.*) in 1898 made a detailed study of the meal worm (*Tenebrio molitor*), and he states that "the middle intestines of three or four hungry worms were triturated with chloroform-water. On allowing the yellow solution to stand overnight with tyrosine, a violet-black coloration was produced, whilst in a solution to which no tyrosine had been added only a slight darkening was observed."

In a repetition of the work, his results have been confirmed by the author, but it has also been found that the more perfectly the body solids were removed from the outer surface of the intestine the less rapidly did the coloration with tyrosine proceed, this being true for either hungry or well-fed larva. The body of the larva is filled with a white semi-solid folded in many convolutions. If this solid is exposed to the air, it rapidly changes through slate to a dense grey-black, and, as will be shown later, it contains some soluble tyrosinase and a large amount of a new "insoluble tyrosinase."

The intestinal juice, obtained by removing the intestine and cleansing it as completely as possible from the body-filling, then grinding with fine quartz in an agate mortar, triturating with chloroform-water, and filtering, does not colour appreciably in twenty-four hours, but later changes through violet to a dense black solution. The action of the fresh extract on tyrosine is slow, but shows the presence of some small amounts of the oxydase; that the oxidising power is due to incomplete removal of the body-filling and not to intestinal juices is the present belief of the author.

Soluble Tyrosinase in the Body-Filling of the Meal Worm.

Twenty-seven grams of the larva were ground in a mortar with chloroform-water, and the milky liquid was strained through

cheese-cloth. The grinding of the residue was repeated until the strainings were no longer milky, and only the hulls of the larva remained in the cloth.

The milky extract, if kept a short time in the air, rapidly darkens at the surface, but remains white where not in contact with oxygen.

The extract was poured into a thin filter paper, and kept, covered with a watch glass, until most of the liquid had filtered through, dropping on solid ammonium sulphate in excess of what was required to produce a saturated solution, this process requiring some hours. In this manner the soluble tyrosinase and the colloidal insoluble tyrosinase, which passed through the first filter, were precipitated together as a light grey, voluminous mass.* This was collected, washed with saturated ammonium sulphate solution, dissolved in distilled water and filtered, reprecipitated with ammonium sulphate, washed with a saturated ammonium sulphate solution, and dissolved in 40 c.c. of 0.05 per cent. sodium carbonate solution, and filtered. The solution so obtained was light brownish-grey, and contained the soluble tyrosinase originally present in the larva. 0.5 c.c. portions of this solution were added to solutions of various reagents, with the results shown in table I. When the tyrosinase solution had been previously heated to 90°, no coloration appeared in any tube, excepting in that containing quinol, showing that perhaps two oxydases were present, tyrosinase being destroyed before 90°, and laccase perhaps surviving the short heating, tyrosinase being almost always accompanied by a laccase-like ferment (Bourquelot, *Compt. rend.*, 1896, 123, 315, 423).

TABLE I.

Action of Soluble Tyrosinase from Larva of Tenebro molitor.

Tube.	Reagent.	Total volume, in c.c.	Time, in hours.	Results.
1.	—	3	72	Unchanged.
2.	Tyrosine	3	24	Violet-black and precipitate.
3.	Tyrosine + 0.001 gram FeSO ₄ .	3	72	Unchanged.
4.	Quinol	3	24	Deep red.
5.	Phenol	3	48	Pink.
6.	p-Aminophenol.....	3	24	Brownish-black.
7.	Guaiacol	3	24	Pink.
8.	Phloroglucinol	3	72	Unchanged.
9.	Resorcinol	3	72	"
10.	Pyramidone	3	72	"

* If the filtered liquid is not precipitated, it very rapidly darkens and soon becomes jet black. The black pigment may be salted out with ammonium sulphate, and appears as a lustrous, black, amorphous mass. It will be investigated later.

When the precipitation of the filtrate is carried out by the addition of three volumes of alcohol instead of saturating with ammonium sulphate, a grey precipitate is obtained very similar in appearance to that produced by the ammonium sulphate, but when this precipitate is dissolved it shows no tyrosinase properties, and only the laccase-like ferment can be found in the alcoholic mother liquor, showing that apparently alcohol is fatal to this variety of tyrosinase.

Insoluble Tyrosinase.

The residue left on the filter from the filtration of the extract of crushed larva (see above) was washed on the filter with chloroform-water during several days. The washing was considered complete when 10 c.c. of the liquid, which had been in contact with the solid (total volume=60 c.c.) for sixteen hours, after being filtered through double "barium" filters, gave no coloration with tyrosine during twenty-four hours.

The solid so obtained is a grey, flocculent mass, which, when dried at 65°, forms 4 to 5 per cent. of the original weight of the live larva. It contains from 1.0 to 1.5 per cent. of ash, consisting chiefly of iron oxide, and containing no manganese which could be detected by the usual tests. The drying process, however, destroys all oxidising activity.

The entire insoluble mass, naturally, cannot be called tyrosinase, as a large percentage of it must be other insoluble body products. The insoluble tyrosinase in this preparation is, however, very active. If the product is washed as above, it may be kept without diminution of activity for months in a tube containing enough chloroform and water ($1\text{CHCl}_3:4\text{H}_2\text{O}$) to cover it completely. When a few drops of this suspension are added to an aqueous solution of tyrosine, the mixture undergoes a series of colour changes, ranging through pink, rose, violet, and blue-black to a deposition of a black, pigment-like substance, and leaving the supernatant liquid completely decolorised. The coloration usually begins in from two to four minutes after the addition of tyrosine, and the series of colour changes is complete in a few hours. If the colourless, supernatant liquid is then removed and more tyrosine solution added, the series of colour changes is repeated. This continual removal and addition of tyrosine solution has been carried out with one specimen of tyrosinase weighing approximately 0.01 gram* for four days, during which the series of colour changes was repeated seven times.

* Where weights of "insoluble tyrosinase used" are given, it means that an aliquot portion of the preparation was dried on a water-bath and weighed. The weights are therefore only an approximation.

That the entire series of colour changes is produced from contact with the insoluble portion and not by a zymogen acting in the presence of tyrosine to set free soluble tyrosinase, was proved by the following experiment.

A portion of insoluble tyrosinase was added to a saturated aqueous solution of tyrosine. In a few minutes the solution had become pink, changing shortly to rose. One half of this solution was now removed and filtered twice through "barium" filters, the other half remaining in contact with the insoluble tyrosinase. The tubes were then set aside in the dark. In a few hours the contents of the tube containing the insoluble tyrosinase and tyrosine solution became changed, first violet, and finally colourless, with the deposition of a black, pigment-like substance. The filtered portion, on the other hand, remained an unchanged rose colour for eighteen days, and was then discarded.

That the tyrosinase was not present in still unruptured cells was proved by grinding the insoluble preparation in an agate mortar with fine quartz until no grit was precipitable. This was then triturated with water, and filtered. The filtered portion gave no coloration with tyrosine in twenty-four hours, whilst the insoluble residue was as active as it was before grinding.

Not only does the insoluble preparation oxidise tyrosine easily, but other phenolic compounds are also acted on to produce the series of colour changes given in table II:

TABLE II.

[Approximately 0.01 gram of insoluble tyrosinase (+ insoluble body products) was used in each test. Volume of 5 c.c. in each.]

Tube.	Reagent added.	Colour series.
1.	—	Colourless after 72 hours.
2.	Tyrosine	Pink → orange-rose → rose → light red → violet → blue-black → insoluble black precipitate.
3.	Pyrogallol	Colourless after 72 hours.
4.	Phloroglucinol	" " "
5.	Resorcinol	" " "
6.	Quinol	" " "
7.	Pyramidone	" " "
8.	Orcinol	" " "
9.	<i>p</i> -Aminobenzaldehyde ...	" " "
10.	<i>p</i> -Nitrosobenzaldehyde ...	" " "
11.	Ethyl <i>p</i> -aminobenzoate ...	" " "
12.	<i>p</i> -Aminophenol	Brown → reddish-brown precipitate.
13.	Guaiaacol	Orange-pink → red → brownish-red.
14.	Gum guaiacum	Rapidly blues.
15.	2:4-Diaminophenol * ...	Pink → orange-pink → orange-brown → orange-red → deep red.

* An aqueous solution of 2:4-diaminophenol changes colour when exposed to the air, but not nearly so rapidly as when insoluble tyrosinase has been added.

In order to test the effect of salts on the system tyrosine-tyrosinase, 0.001 gram of various salts was added to tubes containing approximately 0.01 gram of insoluble tyrosinase and 5 c.c. of a saturated aqueous solution of tyrosine, and the tubes were kept for some time.

In those tubes to which had been added potassium cyanide, mercuric chloride, copper sulphate, uranyl chloride, and ferrous sulphate, no coloration was observed during sixteen hours. The addition of manganous sulphate, potassium nitrite, barium chloride, potassium oxalate, strychnine, or atropine had no effect on the progress of the coloration, whilst sodium arsenate, starch, and starch and potassium iodide had a marked effect in that the rose coloration appeared more rapidly and remained much longer and deeper in colour than in the case of the untreated solution. The portion treated with starch and potassium iodide became intense red,* whilst the untreated solution was only light pink. Warming the solution to 75° for a short time prevents all coloration when it is subsequently treated with tyrosine, starch, and potassium iodide.

Action of Glycerol on Insoluble Tyrosinase.

Various attempts were made to preserve the ferment in glycerol rather than in chloroform-water since Gessard (*loc. cit.*) recommends this method, but in every instance the preparation was rendered inactive. In order further to test the effect of glycerol, the author proceeded as follows. One gram of live larva was ground with chloroform-water and filtered through cheese-cloth. To the filtrate (3 c.c.) was added two volumes of glycerol and solid tyrosine. No coloration appeared in twelve hours. The solution was then diluted with water to 36 c.c., and kept for a further period of twenty-four hours without a trace of coloration appearing; a further dilution to 65 c.c. caused no change in seventy-two hours more. Without the addition of glycerol the coloration proceeds very rapidly even in the absence of added tyrosine. Addition of glycerol to the washed insoluble tyrosinase and keeping the mixture for a few hours caused a total loss of the activity of the preparation even when subsequently washed free from glycerol.

Occurrence of a Laccase-like Ferment in the Larva of Tenebrio molitor.

It was early noticed in the progress of this work that quinol was rapidly oxidised by the unwashed body-filling of the larva and

* No iodine was liberated in 48 hours.

not by the washed insoluble tyrosinase. If the washings are heated rapidly to boiling, the resulting precipitate collected, and the filtrate then evaporated at 30—40°, an oily solid is deposited which is very active in oxidising quinol, but does not affect tyrosine. This oxydase is much more resistant to heat than tyrosinase, and may be heated at 100° for some minutes without losing much of its activity. Prolonged heating, however, gradually causes it to lose its oxidising power.

The Chromogen occurring in the Larva of Tenebro molitor.

As has been previously stated, the body fluid of the meal worm, when exposed to the action of the air, rapidly darkens under the influence of the tyrosinase contained in it and oxygen, to form a dense, black solution. The formation of this coloration shows that a chromogen must be present in the body-filling of the larva, and attempts were made to isolate it.

Five grams of the larva were ground with chloroform-water and filtered through cheese-cloth. The filtrate (150 c.c.) was warmed on a water-bath to 85° to destroy all tyrosinase and to coagulate the insoluble products, albumen, etc. After a few minutes' heating, the mixture was filtered, and the filtrate precipitated with basic lead acetate, again filtered, and lead removed from the filtrate by hydrogen sulphide. The clear filtrate was evaporated to dryness on a water-bath. The product, so obtained, is a light yellow resin, completely soluble in 0.05 per cent. sodium carbonate (3 c.c.), giving a yellow solution. When three drops of this solution are added to water, containing insoluble tyrosinase (total vol. 2 c.c.), a mixture is obtained giving identical colour changes to those obtained from a tyrosine solution, namely, pink, through rose, violet, and blue-black, a black precipitate being finally formed. The amount of the chromogen so obtained was very small, but an attempt will be made to prepare larger quantities in the near future. From the evidence at hand, however, the chromogen appears to be either tyrosine or a closely allied compound. No coloration is produced by the addition of laccase.

Occurrence of Tyrosinase in Other Animal Bodies.

Two examples of myriopods, *Scalopocryptops sexpinosa* and *Julius canadensis*, Newp., were examined for the presence of tyrosinase, and in both instances an abundance of the ferment was found. The entire body was ground with sand in an agate mortar, extracted with chloroform-water, and filtered. This fluid was divided into three parts, one containing no added material, one

tyrosine, and one phenol. In a few hours the portion containing tyrosine had changed through violet to blue-black, with the deposition of a black, melanin-like substance. The portion containing phenol changed through orange to deep sepia, whilst the untreated tubes remained colourless. Boiling prevents all coloration.

Tyrosinase was also found to be very abundant in the larva of *Cucujus clavipes*,* changing tyrosine solution through pink to rose, violet, blue-black to melanin, and phenol through rose to light red and crimson.

Occurrence of a Quinol-oxidising Ferment in Vertebrate Animal Tissues.

It has long been observed (Baumann and Preusse, *Zeitsch. physiol. Chem.*, 1879, **3**, 156) that after the use of phenol the urine assumes a dark colour on exposure to the air (the so-called "carbolic urine"), from which quinol, quinolsulphonic acid, and quinol-decomposition products may be isolated. The same coloration occurs after the administration of quinol.

The author has observed that this coloration is not peculiar to the urine, but that extracts of practically all the tissues rapidly oxidise quinol to intensely coloured solutions. Among the animals investigated were young rats, mice, albino rats, kittens, chickens, etc., and in each instance a rapid oxidation was produced with extracts of the heart, liver, lungs, brain, kidneys, spleen, pancreas, testes, ovary, skeletal muscles, skin, and blood serum; in every case the coloration being most intense when blood serum was used. Long-continued boiling causes a gradual loss in oxidising power, although a very short heating seems to increase the activity.

Different extracts gave different colorations in similar circumstances, and these changes are shown in table III. The tissues were ground with sand, triturated with chloroform-water, and filtered. To the turbid filtrate, quinol was added, and the tube set aside in an oven at 40°.†

No coloration was observed in any case in "blank" tubes, or in tubes treated with tyrosine or guaiacol. In all cases the final coloration obtained with quinol was either deep blood-red or reddish-brown verging on black.

When quinol was injected subcutaneously in a kitten, and the animal killed after three to four hours, the post-mortem examination showed a red circle under the skin where the injection was

* Identified through the courtesy of Dr. A. D. Hopkins, of the Bureau of Entomology, The United States Department of Agriculture.

† The coloration is decidedly more rapid at 40° than at room temperature.

TABLE III.

Tube.	Organ.	Origin.	Time, in hours.	Result.
1.	Skin	Young rat ...	12	Claret-coloured solution.
2.	„	„ „ ...	24	Deep red solution.
3.	„	Albino rat ...	24	„ „
4.	„	„ „ ...	24	Brown solution (had been first heated to 100°).
5.	Spleen.....	„ „ ...	24	Red solution.
6.	Kidney	„ „ ...	24	Rose „ (after 48 hours, red).
7.	Pancreas.....	„ „ ...	48	Rose solution.
8.	Lungs	„ „ ...	48	„ „
9.	Liver	„ „ ...	48	„ „
10.	„ (boiled)...	„ „ ...	48	Light pink solution.
11.	Testes	„ „ ...	48	Deep red „
12.	Muscle	„ „ ...	48	Pink „
13.	Brain	„ „ ...	48	Deep brown „
14.	Bile.....	Chicken	16	Brown „
15.	„	„	24	Black „
16.	Liver	„	16	Deep red „
17.	Brain	„	16	Reddish-brown solution.
18.	Ovary	„	16	„ „ „
19.	Blood serum ...	„	16	Reddish-black „
20.	Pancreas.....	„	16	Brownish-black „
21.	Spinal cord.....	Grey rat	16	Bright red „
22.	Brain	„	16	Dull reddish-brown solution.

made. The remainder of the under surface of the skin and the flesh were normal in colour, but on exposure to the air the skin tissue and the muscles rapidly turned pink. The blood-serum also soon became deep red, although, when expressed from the clot, it was of normal colour.

Occurrence of Laccase and Tyrosinase in the "Indian Pipe"
(*Monotropa uniflora*).

Gautier (*loc. cit.*) found that many plants which blacken during the process of drying contain a tyrosine-oxidising ferment. The common *Monotropa uniflora*, of the north-eastern portion of the United States, presents this peculiarity, and an effort was made to discover whether or not this plant could be used as a source of tyrosinase.

A chloroform-water extract of the crushed plants was precipitated with five volumes of 95 per cent. alcohol. The violet-coloured precipitate so obtained was collected after twenty-four hours, and redissolved in 0.05 per cent. sodium carbonate solution. The solution was found to have some oxidising power, slowly oxidising tyrosine to a blue-black insoluble substance. The action on quinol was very rapid, however, the solution becoming deep red. Boiling destroyed the power of oxidising tyrosine, but not

the power of oxidising quinol, showing that the major portion of the oxydase is evidently laccase. Tincture of gum guaiacum is rapidly turned blue, whilst guaiacol is turned pink by the action of the solution.

If the fresh plants are crushed with three parts by weight of glycerol, and the mixture kept for eighteen hours and then filtered by the aid of the pump, a clear, greenish-blue solution is obtained, which, after a long time, becomes an intense bluish-black.

Two drops of this filtrate almost instantly turns tincture of gum guaiacum blue, and oxidises tyrosine, which changes colour through pink to rose, violet, and finally blue-black. Quinol exhibits, under its influence, colour changes from orange to brown, deep reddish-brown, and finally intense red. When the solution of the oxydase has previously been warmed to 80°, it is without effect on tyrosine solution. From these data, it is evident that both tyrosinase and laccase are present in the plant, but the quantity of tyrosinase is small compared with that found in certain of the *Russula*.

Summary.

1. A new variety of tyrosinase has been discovered and investigated.

2. This variety is distinguished from the known tyrosinases by its insolubility in water, its loss of vitality in glycerol solutions and on drying, and by its inability to oxidise resorcinol, orcinol, etc.

3. A chromogen has been found in the larva of *Tenebro molitor*, giving with tyrosinase colour reactions identical with those given by tyrosine.

4. Tyrosinase has been found in the myriopods *Scalopocryptops sexpinosa* and *Julius canadensis*, Newp., and also in the larva of *Cucujus clavipes*.

5. It has been observed that extracts of almost all animal tissues possess the power of oxidising solutions of quinol, and that this power is considerably diminished by prolonged boiling.

6. Tyrosinase has been found to exist together with laccase in the *Monotropa uniflora*.

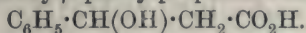
THE CARNEGIE INSTITUTION OF WASHINGTON,
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XIV.—*Experiments on the Walden Inversion. Part III.*
Optically Active β -Hydroxy- β -phenylpropionic Acids
and the Corresponding β -Bromo- β -phenylpropionic
Acids.

By ALEX. MCKENZIE and HERBERT BROOKE PERREN HUMPHRIES.

THE effect, which in certain cases is associated with the electro-negative phenyl group, has been brought out clearly in previous work on the Walden inversion (McKenzie and Clough, *Trans.*, 1908, 93, 811; 1909, 95, 777). For example, *l*-phenylchloroacetic acid, $\text{C}_6\text{H}_5\cdot\text{CHCl}\cdot\text{CO}_2\text{H}$, is converted into a mixture of *r*- and *l*-mandelic acids when aqueous sodium hydroxide is used to displace the chlorine atom by the hydroxy-group; a mixture of *r*- and *d*-mandelic acids is, however, produced when silver carbonate is substituted for sodium hydroxide. This behaviour makes the problem of the Walden inversion more complicated than before, for this reason that, by analogy with previous work of Walden and others, it was to have been expected that sodium hydroxide should have caused the formation of a *dextro-rotatory* mandelic acid mixture from the *laevorotatory* chloro-acid, and that silver carbonate should have caused the formation of a *laevo-rotatory* mandelic acid mixture. The contrast between the inter-conversion of the active lactic acids, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, on the one hand, and the interconversion of the active mandelic acids, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$, on the other, by the Walden inversion, is very striking, and must be taken into account in any interpretation regarding the mechanism of the action which may be advanced.

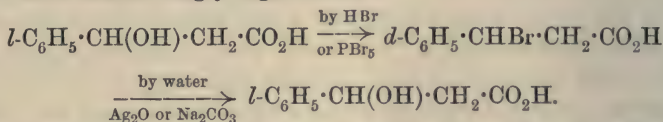
The present research is concerned with changes undergone by the optically active β -hydroxy- β -phenylpropionic acids,



One of the objects was to find out if any Walden inversion could be detected in the course of changes undergone by a compound where the carboxyl group is not attached directly to the asymmetric carbon atom. Meanwhile this problem has been investigated by E. Fischer and Scheibler (*Ber.*, 1909, 42, 1219), who studied the displacement of the hydroxy-group in *l*- β -hydroxybutyric acid, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. By the action of phosphorus pentachloride, this acid was converted into *d*- β -chlorobutyric acid, from which the original *l*-hydroxy-acid was regenerated by displacing the chlorine by means of a number of different agents.

Bearing in mind the possibility of the phenyl group exerting an influence entirely different from that of the methyl group, we prepared the optically active β -hydroxy- β -phenylpropionic acids by the resolu-

tion of the inactive acid with morphine in aqueous solution. When the *l*-acid is acted on by hydrobromic acid, the resulting bromo-acid is dextrorotatory, and the change is accompanied by a certain amount of racemisation, which is less pronounced when the temperature at which the displacement occurs is kept low. The behaviour of the *d*-hydroxy-acid towards hydrobromic acid is, of course, similar. Phosphorus pentabromide also brings about a change of sign of rotation by its action on the active hydroxy-acids. When the bromine in the active bromo-acids is displaced by the hydroxy-group, either by means of silver oxide and water, or by sodium carbonate and water or by water alone, a change of sign of rotation again occurs. The parent acid is accordingly regenerated:



The displacement of the hydroxy-group in the active β -hydroxy- β -phenylpropionic acids by the bromine atom appears to be a normal action, since both phosphorus pentabromide and hydrobromic acid act in a similar manner, and since a change of sign also accompanies the action of hydrobromic acid on the methyl *d*-ester.

There is, therefore, no evidence of the occurrence of a Walden inversion in any of the changes studied.

EXPERIMENTAL.

Resolution of Inactive β -Hydroxy- β phenylpropionic Acid.

Inactive β -hydroxy- β -phenylpropionic acid was prepared by the action of boiling water on inactive β -bromo- β -phenylpropionic acid, which is readily obtained from hydrobromic acid and cinnamic acid (Fittig and Binder, *Annalen*, 1879, 195, 131).

The resolution by means of morphine proceeds with exceptional ease. So far as we are able to judge, it is immaterial whether synthetic or storax cinnamic acid is used as the starting point for the preparation of the inactive acid.

Powdered morphine (61 grams) was added to a solution of 36 grams of the hydroxy-acid in 750 c.c. of boiling water. Crystallisation began after the solution was allowed to cool at the ordinary temperature for one hour; the solution was then stirred occasionally, and left overnight at the ordinary temperature. About half of the total morphine salt separated. The crystals, which melted and decomposed at about 206° , were suspended in 50 c.c. of water and the morphine precipitated by means of a slight excess of ammonia. The addition of an excess of hydrochloric acid to the filtrate, from which the morphine

had been separated, caused the gradual separation, in the form of needles, of the *l*-acid, which is sparingly soluble in water. The acid was drained off and, after crystallisation from 300 c.c. of benzene, was pure. The yield amounted to 9 grams. Its melting point and its specific rotation did not alter after it had been recrystallised several times from benzene.

l- β -Hydroxy- β -phenylpropionic acid, $C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, is sparingly soluble in water and in benzene. It separates in colourless needles and melts at 115—116°:

0.1925 gave 0.4579 CO_2 and 0.1032 H_2O . $C = 64.9$; $H = 6.0$.

$C_9H_{10}O_3$ requires $C = 65.0$; $H = 6.1$ per cent.

Its rotation was determined in ethyl-alcoholic solution:

$$l = 2, c = 5.153, \alpha_D^{20} - 1.95^\circ, [\alpha]_D^{20} - 18.9^\circ.$$

In order to obtain the enantiomorphously related isomeride, the mother liquor, from which the morphine *l*-salt had been separated, was concentrated by evaporation to 150 c.c., when no separation of salt took place. The dextro-acid was then separated in the manner described above and crystallised from benzene. The yield amounted to 10 grams.

d- β -Hydroxy- β -phenylpropionic acid melts at 115—116°, and resembles its *l*-isomeride in other particulars:

0.194 gave 0.4638 CO_2 and 0.1051 H_2O . $C = 64.9$; $H = 6.0$.

$C_9H_{10}O_3$ requires $C = 65.0$; $H = 6.1$ per cent.

A determination of its specific rotation in ethyl-alcoholic solution gave a value in agreement with that of the *l*-acid:

$$l = 2, c = 5.194, \alpha_D^{18} + 1.99^\circ, [\alpha]_D^{18} + 19.2^\circ.$$

Although the inactive acid had not been resolved previously, the active acids have been obtained by Barkow (*Inaug. Diss.*, Strasburg, 1906), working in Erlenmeyer's laboratory, in the course of an investigation dealing with the α -halogen- β -hydroxy- β -phenylpropionic acids. Barkow found that when *d*- α -bromo- β -hydroxy- β -phenylpropionic acid, $C_6H_5 \cdot CH(OH) \cdot CHBr \cdot CO_2H$, was reduced by sodium amalgam, it was converted into *d*- β -hydroxy- β -phenylpropionic acid with $[\alpha]_D + 19^\circ$ in ethyl-alcoholic solution.

Action of Hydrobromic Acid on the Active β -Hydroxy- β -phenylpropionic Acids.

Attempts to resolve inactive β -bromo- β -phenylpropionic acid into its optically active isomerides were not promising. The bases employed caused some decomposition of the bromo-acid into styrene. The active bromo-acids were accordingly obtained from the corresponding

hydroxy-acids, but they underwent partial racemisation in the process of their formation by this method.

The *l*-hydroxy-acid (2.5 grams) was covered with aqueous hydrobromic acid, which had previously been saturated at 0°. The hydroxy-acid dissolved, and the bromo-acid separated. After one hour, water was added, the sparingly soluble acid drained off, washed with water, and dried over soda-lime under diminished pressure. The product had $[\alpha]_D + 16.8^\circ$ for $c = 2.029$ in ethyl-alcoholic solution. It was a mixture of the *r*- and *d*-bromo-acids, since its melting point was indefinite and its rotation changed on crystallisation. The effect of crystallising three times from carbon tetrachloride was to give an acid mixture, which contained more of the inactive form than before, the value for its rotation in ethyl-alcoholic solution being $[\alpha]_D + 8.5^\circ$ for $c = 2.05$.

If the fuming hydrobromic acid is shaken with the *l*-hydroxy-acid for a few minutes only at the laboratory temperature, the racemisation is less pronounced. In one experiment, for example, the crude bromo-acid, obtained from the *l*-hydroxy-acid, was crystallised once from carbon tetrachloride, and then gave $[\alpha]_D + 20.6^\circ$ for $c = 2.204$ in ethyl-alcoholic solution.

When the *d*-hydroxy-acid was shaken with aqueous hydrobromic acid, saturated at 0°, for two or three minutes at 0°, the crude bromo-acid which separated had $[\alpha]_D - 23.9^\circ$ for $c = 2.974$ in ethyl-alcoholic solution.

Obviously, therefore, the amount of racemisation could be lessened by maintaining the temperature low during the action of the hydrobromic acid. Forty c.c. of aqueous hydrobromic acid (saturated at 0°) were accordingly cooled to -10° , and 8.5 grams of the *l*-hydroxy-acid added. The rapid solution of the hydroxy-acid was succeeded by the separation of a voluminous crop of the bromo-acid. After five minutes, the crystals were separated, washed with a little water, and dried. The product melted indefinitely at $126-133^\circ$, and had $[\alpha]_D + 32.2^\circ$ for $c = 2.125$ in ethyl-alcoholic solution. It was crystallised from 65 c.c. of chloroform, and the crop which separated (6 grams) had $[\alpha]_D + 21^\circ$. From the mother liquor, two successive crops were withdrawn, the second of which (1.1 gram) had $[\alpha]_D + 58.3$ for $c = 1.03$ in ethyl-alcoholic solution, whilst the residual mother liquor yielded 2 grams of acid with $[\alpha]_D + 96.2^\circ$ for $c = 1.107$ in ethyl-alcoholic solution. An estimation of bromine in the latter acid indicated the presence of cinnamic acid together with the bromo-acid.

The pure active bromo-acids have accordingly a value for their specific rotation higher than 96.2° , and appear to be more readily soluble in most solvents than the inactive isomeride. Further attempts to isolate them were not made, since the points of interest,

from the point of view of this investigation, could be established by aid of the partly-racemised acids.

The *d*-hydroxy-acid gave similar results to the above when it was treated with fuming hydrobromic acid at -10° .

Action of Phosphorus Pentabromide on the l-Hydroxy-acid.

The *l*-acid was dissolved in a mixture of chloroform and ether and acted on with an excess of phosphorus pentabromide, the temperature being maintained low. The bromo-acid, obtained after decomposition of the acid bromide with water, gave $[\alpha]_D + 14.4^{\circ}$ for $c = 2.39$ in ethyl-alcoholic solution.

Thus phosphorus pentabromide behaves like hydrobromic acid in causing a change of sign of rotation when it acts on the active hydroxy-acid. As is usually the case when a phosphorus halide acts on an active hydroxy-acid, the formation of the halogen acid is accompanied by partial racemisation.

Formation of l-Bromo-ester from d-Hydroxy-ester.

d- β -Hydroxy- β -phenylpropionic acid was converted into its methyl ester by the Fischer-Speier method. This ester, which had $[\alpha]_D + 14.1^{\circ}$ for $c = 4.717$ in ethyl-alcoholic solution, was added to an excess of fuming hydrobromic acid at -10° , and, after shaking for five minutes, the bromo-ester was separated. It was laevorotatory, giving $[\alpha]_D - 28.5^{\circ}$ for $c = 6.654$ in ethyl-alcoholic solution.

The action of phosphorus pentabromide on the *d*-hydroxy-ester was also examined, the bromination being effected in dry chloroform and at a low temperature. The resulting bromo-ester was again laevorotatory, giving $[\alpha]_D - 4.6^{\circ}$ for $c = 3.03$ in ethyl-alcoholic solution.

Displacement of Bromine in the d-Bromo-acid by the Hydroxy-group.

A mixture of the dextro- and inactive bromo-acids (0.4 gram) with $[\alpha]_D + 58.3^{\circ}$ was added to water (10 c.c.), and, after five days at the ordinary temperature, the solution was heated for a few minutes until the odour of styrene had disappeared. The product was then evaporated to dryness at the ordinary temperature under diminished pressure. The residue gave the value $[\alpha]_D - 7.7^{\circ}$ for $c = 2.27$ in ethyl-alcoholic solution.

A mixture of the dextro- and inactive bromo-acids (0.7 gram) with $[\alpha]_D + 58.3^{\circ}$ was added to a solution of 0.4 gram of sodium carbonate in 10 c.c. of water. After five days, the small amount of styrene present was removed. On acidification with hydrochloric acid, there

was no appreciable separation of cinnamic acid. The hydroxy-acid was extracted with ether, and had the specific rotation $[\alpha]_D - 5.5^\circ$ for $c = 1.451$ in ethyl-alcoholic solution.

Silver oxide, obtained from 1 gram of silver nitrate, was added to the dextrorotatory bromo-acid (0.7 gram) with $[\alpha]_D + 96.2^\circ$ and 10 c.c. of water. After twenty-four hours, with occasional shaking, the product was treated with hydrochloric acid, filtered, and the filtrate extracted with ether. The resulting hydroxy-acid gave the value $[\alpha]_D - 13.7^\circ$ with $c = 1.17$ in ethyl-alcoholic solution.

In these cases, therefore, using either water alone, sodium carbonate and water, or silver oxide and water, the hydroxy-acid recovered is opposite in sign to that of the bromo-acid used, and of the same sign as the parent hydroxy-acid from which the bromo-acid was obtained.

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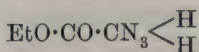
XV.—*The Triazo-group. Part XI. Substituted Triazomalonic and Phenyltriazooacetic Acids.*

By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

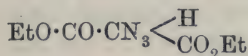
PURSUING our study of the effect produced by environment on the behaviour of the triazo-group, we deal in the present communication with substituted triazomalonic acids, for the purpose of comparison with the series of monobasic fatty acids already considered in previous papers (Trans., 1908, 93, 72; 1909, 95, 191). It has been shown that the characteristic manner in which triazoacetone is decomposed by alkalis may be deeply modified by exchanging the unsubstituted methyl group for ethoxyl, the azidic radicle in triazoacetic ester and its homologues being quite indifferent towards alkali, the attack of which is resisted even by the triazo-acids themselves unless considerable excess of the agent is employed and the temperature raised to 50° or more. From the fact that in the series quoted, α -triazoisobutyric acid escaped altogether, it was concluded that the limiting condition for elimination of two-thirds the azidic nitrogen from triazo-acids depends on the association of hydrogen with the carbon atom which carries the triazo-group.

Accepting ethyl triazoacetate as a standard, the series of substituted triazomalonic esters described in this paper may be regarded as derived by replacing one or both atoms of hydrogen with carboxyethyl,

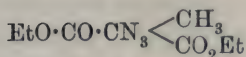
alkyl, phenyl, or triazidic groups, as represented by the following constitutional formulæ :



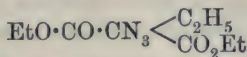
Ethyl triazoacetate.



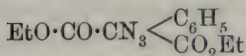
Ethyl triazomalonate
(not isolated).



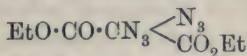
Ethyl methyltriazomalonate.



Ethyl ethyltriazomalonate.



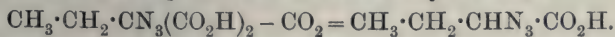
Ethyl phenyltriazomalonate.



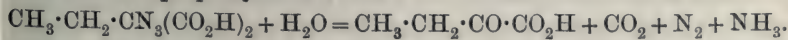
Ethylbistriazomalonate.

The first point to notice in connexion with the above series is that the introduction of a second carboxyethyl group into the molecule of triazoacetic ester disturbs so profoundly the equilibrium of the molecule that ethyl triazomalonate is not capable of separate existence. All attempts to prepare this compound by variations of the original process for obtaining triazo-esters have been fruitless, not from want of reactivity between sodium azide and the halogen of the substituted malonate, but because under those circumstances in which double decomposition can be brought about, the product immediately undergoes profound decomposition, and gives rise to nitrogen, ammonia, and hydrazoic acid, along with a solid nitrogenous compound of high molecular weight. As soon as the remaining hydrogen atom is replaced, however, whether by alkyl, phenyl, or the triazo-group, stability returns to the molecule, and the substituted triazomalonate ester is sufficiently cohesive not only to withstand the action of alkali, but actually to undergo hydrolysis, furnishing the substituted triazomalonate acid.

In the alkyltriazomalonate acids we have to deal with substances directly comparable with α -triazoisobutyric acid, inasmuch as the triazotised carbon atom is tertiary. Accordingly they display unusual resistance towards alkali, which depends for the success of its attack on the well known power of substituted malonic acids to lose one molecule of carbon dioxide. Making this alteration in ethyltriazomalonate acid, for example, leads to α -triazobutyric acid :



Consequent on this, there occurs elimination of two-thirds the azidic nitrogen, so that the net result of decomposing ethyltriazomalonate acid with alkali is propionylformic acid :

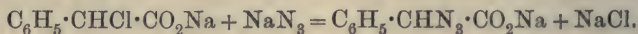


Proceeding now to consider the effect of the phenyl group, an increase in the reactivity of the molecule is to be noted, and although it has proved possible to hydrolyse the ester to phenyltriazomalonate

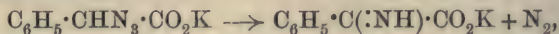
acid, and by the action of ammonia to prepare phenyltriazomalonamide, nevertheless the further breakdown to benzoylformic acid is accomplished more readily than the corresponding degradation of the purely aliphatic molecule:



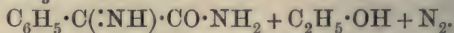
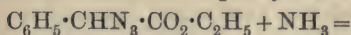
This access of reactivity is shown still more clearly by the behaviour of phenyltriazooacetic ester, which we have prepared for comparison with triazoacetic ester. Whilst the latter substance may be hydrolysed to the acid without risk of eliminating the two-thirds nitrogen, phenyltriazooacetic ester is so sensitive towards alkali that the acid cannot be prepared by hydrolysis, but must be derived from sodium phenylchloroacetate by double decomposition with sodium azide:



By proceeding carefully it is possible to arrest decomposition of phenyltriazooacetic acid with alkali at the stage intermediate between the original substance and benzoylformic acid, namely, potassium phenyliminoacetate:



but this compound readily suffers hydrolysis to potassium benzoylformate and ammonia. The instability of phenyltriazooacetic ester is illustrated still better by its behaviour towards ammonia, which converts it into phenyliminoacetamide with loss of two-thirds nitrogen and without formation of phenyltriazooacetamide.

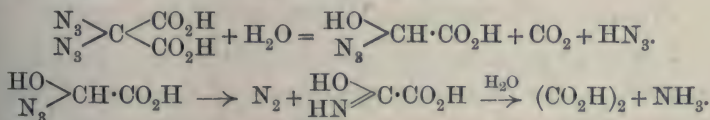


The latter substance, in fact, could not be isolated, although the transformation of triazoacetic ester [into triazoacetamide by the direct action of ammonia is practically quantitative.

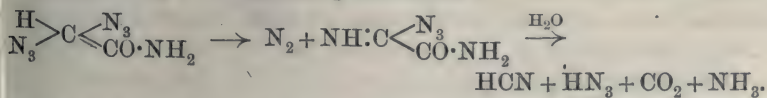
Proceeding now to the bistriazo-derivatives, we are confronted with another illustration of the comparative immunity of the triazo-group when the carbon atom which carries it is tertiary. In studying the properties of bistriazoacetic ester (Trans., 1908, 93, 1073), it was found that potassium hydroxide readily eliminates hydrazoic acid, and that even ammonia brings about this change too rapidly to permit the production of bistriazoacetamide; moreover, during the preparation of the ester it was noticed that the double decomposition between dichloroacetic ester and sodium azide was accompanied by continuous liberation of hydrazoic and prussic acids, indicating subsidiary changes which reduced the yield very much below that required by theory. Bistriazomalononic ester, on the other hand, is a comparatively stable substance, and, although exploding with some violence at 180°, is much less dangerous to handle than bistriazoacetic ester. Ammonia converts

it into bistriazomalonic acid, and although this change is accompanied by elimination of hydrazoic acid, the isolation of a solid amide represents a distinct superiority to the behaviour of the bistriazoacetic ester. As might be expected, however, the amide is much more sensitive towards concentrated sulphuric acid than methyltriazomalonic acid and ethyltriazomalonic acid, and is completely broken down by potassium hydroxide, yielding nitrogen and ammonia with prussic and hydrazoic acids.

An attempt to produce bistriazomalonic acid by cautious hydrolysis leads us to believe that this substance, like triazomalonic acid, is capable of existing in solution, but not in the individual state. An ethereal solution was concentrated without heating, but thereby acquired a powerful odour of hydrazoic acid, which remained noticeable during many days' exposure to reduced pressure; a few crystals of oxalic acid separated, and the oil, when quite free from hydrazoic acid, gave a nitrogen percentage agreeing fairly well with that of triazoglycollic acid, this indication being further confirmed by analysis of the barium salt. It appears probable, therefore, that bistriazomalonic acid undergoes the following changes in solution:



The production of prussic acid during the disruption of the triazo-group appears to be a feature of bistriazo-derivatives exclusively, and we have searched again for this compound among the products of decomposing with alkali those triazo-acids and triazo-esters which have been described in previous papers, with a negative result; it is, however, noteworthy that phenyltriazomalonic acid, when warmed with alkali, gives a distinct odour of phenylcarbylamine. It is difficult to explain the formation of prussic acid from bistriazomalonic acid unless the production of the substance is preceded by the loss of carbon dioxide, which would lead to bistriazoacetamide; this might be expected to lose two-thirds the nitrogen of one azidic group, yielding a highly unstable molecule which would become resolved into ammonia with hydrazoic, carbonic, and prussic acids:



Such a change appears more probable when it is recalled that Conrad and Bruckner have shown that dichloroacetamide is among the products of treating dichloromalonic ester with ammonia (*Ber.*, 1891, 24, 2994).

Much remains to be learned, however, in connexion with those bistriazo-compounds in which both azidic groups are attached to the same carbon atom, other points in addition to those mentioned serving to emphasise the characteristic behaviour of such substances. Bistriazomalonic ester, for example, is remarkably stable, and does not appear to undergo alteration with lapse of time, whilst bistriazo-acetic ester develops the odour of prussic acid and deposits, in the course of a few months, massive, transparent crystals (m. p. 91°) containing more carbon, but less nitrogen, than the original material. This rearrangement will be investigated further, as there doubtless occurs some change comparable with the triazole formation which takes place in the molecule of allylazoimide (Trans., 1908, 93, 1174), and with the production of 1-hydroxy-5-phenyltetrazole from benz-hydroximic chloride and sodium azide (Trans., 1909, 95, 183); the recent observation of Schroeter (*Ber.*, 1909, 42, 2336), who obtained diphenyltetrazole from diphenylbistriazomethane, belongs, probably, to the same class of transformation.

EXPERIMENTAL.

Interaction of Chloromalonic Ester and Sodium Azide.

Fifty grams of chloromalonic ester (b. p. $91^{\circ}/2$ mm.) were heated under reflux on the water-bath with 25 grams of alcohol, 20 grams of sodium azide, and sufficient water to maintain the salt in solution; the mixture rapidly became yellow, then dark red, while brisk effervescence was set up, the escaping gases being nitrogen, ammonia, and hydrazoic acid. After four hours the liquid was allowed to cool, and filtered from 3 grams of crystalline material, of which a further quantity about equal to the first was obtained by removing esters in a current of steam, concentrating the residue to about 200 c.c., and then adding dilute sulphuric acid. The substance was purified by precipitation with sulphuric acid from the solution in sodium carbonate, followed by successive recrystallisation from boiling alcohol and ethyl acetate independently, approximately one litre of the latter solvent being required by 0.5 gram; it crystallised in minute, colourless needles, became deep red at about 220° , and decomposed completely in the neighbourhood of 240° . Many analyses have been made, of which the following are typical, without, however, revealing the identity of this compound, but they point consistently to a molecule arising by condensation of two or more molecules of triazomalonic ester:

0.2061 gave 0.3577 CO_2 and 0.0908 H_2O . $\text{C} = 47.29$; $\text{H} = 4.90$.

0.1181 „ 13.2 c.c. N_2 at 20° and 746.5 mm. $\text{N} = 12.56$.

$(\text{C}_9\text{H}_{11}\text{O}_5\text{N}_2)_x$ requires $\text{C} = 47.58$; $\text{H} = 4.84$; $\text{N} = 12.33$ per cent.

The substance is very sparingly soluble in boiling water, alcohol, chloroform, and ethyl acetate; it does not reduce ammoniacal silver oxide, and does not give any characteristic coloration when ferrous sulphate is added to a very dilute solution in sodium hydroxide, but a solution in cold absolute alcohol, which of necessity contains only a minute portion of the substance, develops an intense violet coloration with ferric chloride.

As regards the preparation of triazomalonic ester, the foregoing experiment was a failure, because not only is the solid product quite distinct from a triazo-compound, but the volatile oil removed by steam was found not to contain nitrogen. Another fruitless attempt to obtain the substance consisted in shaking during twenty hours at laboratory temperature a suspension of chloromalonic ester (50 grams) in aqueous alcohol containing sodium azide (20 grams); the mixture became dark red, and pressure was developed, but the odour of ammonia or hydrazoic acid was not perceptible, and the heavy oil which remained undissolved consisted of original material.

Having found that sodium phenyltriazooacetate may be prepared from the chloro-compound by the action of aqueous sodium azide, 25 grams of bromomalonic acid were neutralised with sodium carbonate, and gently warmed with 10 grams of sodium azide dissolved in water. It soon became evident that double decomposition had occurred, because a test with 40 per cent. potassium hydroxide gave torrents of nitrogen and ammonia, but on extracting the acidified solution with ether, and evaporating the solvent under reduced pressure, hydrazoic acid was liberated continuously, leaving an oil which no longer evolved nitrogen when treated with alkali.

Methyltriazomalonic Acid, $\text{CH}_3\cdot\text{CN}_3(\text{CO}_2\text{H})_2$.

Five grams of methyltriazomalonic ester were shaken with 5 grams of potassium hydroxide dissolved in 5 c.c. of water until, after about twenty minutes, the oil had disappeared, when the liquid was gradually acidified with 50 per cent. sulphuric acid and extracted with ether. The residue from the latter solidified in the desiccator, and, after crystallisation from warm benzene, was redissolved in its own weight of ethyl acetate; on adding benzene in approximately equal volume, there separated stellate aggregates of long, transparent prisms melting at $87\cdot5^\circ$:

0.1551 gave $37\cdot0$ c.c. N_2 at 22° and 743 mm. $\text{N} = 26\cdot40$.

$\text{C}_4\text{H}_5\text{O}_4\text{N}_3$ requires $\text{N} = 26\cdot41$ per cent.

The acid is very hygroscopic, and dissolves freely in ethyl acetate; benzene dissolves it only sparingly, however, and it is insoluble in petroleum. Concentrated sulphuric acid attacks the substance

very slowly, whilst stannous chloride in hydrochloric acid liberates nitrogen immediately.

The silver salt was precipitated by silver nitrate from aqueous ammonium methyltriazomalonate, and, although colourless when fresh, rapidly darkened on attempting to recrystallise it from warm water; a small quantity of the dried substance detonated with considerable violence when thrown on a hot plate.

Ethyl Methyltriazomalonate, $\text{CH}_3 \cdot \text{CN}_3(\text{CO}_2 \cdot \text{C}_2\text{H}_5)_2$.

Fifty grams of methylbromomalonate in 30 c.c. of absolute alcohol were heated under reflux during ten hours with 22 grams of sodium azide in 30 c.c. of water; action being then complete, a considerable quantity of water was added, and the precipitated oil distilled under diminished pressure, the principal fraction (32 grams) boiling at $69^\circ/0.6$ mm.:

0.1328 gave 23.0 c.c. N_2 at 17° and 749 mm. $\text{N} = 19.80$.

$\text{C}_8\text{H}_{13}\text{O}_4\text{N}_3$ requires $\text{N} = 19.53$ per cent.

Ethyl methyltriazomalonate is a colourless liquid having sp. gr. 1.11695 at $16^\circ/16^\circ$; it has a faint, agreeable perfume, suggesting acetoacetic ester, and the vapour when inhaled with steam produces an effect on the blood-pressure similar to that of the esters in the monobasic series. As already indicated, cold concentrated potassium hydroxide merely hydrolyses the ester, provided that the alkali is not in great excess and the mixture is not heated; even on evaporating to dryness, the liberation of gas is very slight, and only a small proportion of nitrogen is removed in the form of hydrazoic acid.

Action of Sulphuric Acid.—As in the case of triazoacetic ester, the interaction with concentrated sulphuric acid is very slow, and only on heating the mixture during a considerable period did the volume of liberated nitrogen reach the calculated amount:

0.2243 gave 26.8 c.c. N_2 at 17° and 747 mm. $\text{N} = 13.62$.

$\text{C}_8\text{H}_{13}\text{O}_4\text{N}_3$ requires $2/3\text{N} = 13.02$ per cent.

Behaviour towards Stannous Chloride.—A solution of stannous chloride in hydrochloric acid is without action on the ester until the temperature reaches about 80° , when a slow but regular effervescence sets in, and is completed in about two hours.

0.3038 gave 36.6 c.c. N_2 at 19° and 742 mm. $\text{N} = 13.51$.

$\text{C}_8\text{H}_{13}\text{O}_4\text{N}_3$ requires $2/3\text{N} = 13.02$ per cent.

Methyltriazomalonamide, $\text{CH}_3 \cdot \text{CN}_3(\text{CO} \cdot \text{NH}_2)_2$.

Five grams of the ester were shaken during two hours with 15 c.c. of concentrated aqueous ammonia, excess of which was removed in the vacuum desiccator after twelve hours had elapsed. The crystalline amide was dissolved in boiling benzene, of which about 400 c.c. were required per gram, separating in long, lustrous needles melting at 137.5° :

0.1330 gave 52.5 c.c. N_2 at 17° and 742 mm. $\text{N} = 44.71$.

$\text{C}_4\text{H}_7\text{O}_2\text{N}_5$ requires $\text{N} = 44.58$ per cent.

Methyltriazomalonamide is readily soluble in warm water, alcohol, and petroleum, but is insoluble in cold benzene. A hydrochloric acid solution of stannous chloride attacks the substance rapidly without being heated, and liberates nitrogen. Concentrated sulphuric acid behaves in a most unusual manner, nitrogen being evolved only slowly even on raising the temperature to 125° , below which there is not any effervescence. A parallel with this remarkable behaviour has been noted quite recently in the case of triphenylmethylazoisimide (Wieland, *Ber.*, 1909, **42**, 3027), the solution of which in concentrated sulphuric acid must be heated to 200° before gas evolution becomes vigorous.

Ethyltriazomalononic Acid, $\text{C}_2\text{H}_5 \cdot \text{CN}_3(\text{CO}_2\text{H})_2$.

Exactly the same procedure was adopted as in the case of methyltriazomalononic acid, and, after crystallisation from hot benzene, the acid was obtained in colourless, rhombic, hygroscopic prisms, melting and decomposing at $105\text{--}107^\circ$:

0.1632 gave 34.4 c.c. N_2 at 22° and 766 mm. $\text{N} = 24.12$.

$\text{C}_5\text{H}_7\text{O}_4\text{N}_3$ requires $\text{N} = 24.28$ per cent.

The acid is attacked readily by concentrated sulphuric acid, and by stannous chloride in hydrochloric acid.

Ethyl Ethyltriazomalonate, $\text{C}_2\text{H}_5 \cdot \text{CN}_3(\text{CO}_2 \cdot \text{C}_2\text{H}_5)_2$.

The ester was prepared from 42 grams of ethylbromomalononic ester, 15 grams of sodium azide, and 45 c.c. of 50 per cent. alcohol, heating under reflux being continued during eight hours; the product was fractionated under reduced pressure, boiling at $83.5^\circ/0.7$ mm.:

0.1670 gave 27.3 c.c. N_2 at 22° and 769 mm. $\text{N} = 18.74$.

$\text{C}_9\text{H}_{15}\text{O}_4\text{N}_3$ requires $\text{N} = 18.38$ per cent.

The colourless liquid has sp. gr. 1.1161 at $16^\circ/16^\circ$, and the vapour,

although characterised by a pleasant odour, has the disagreeable effect on the blood-pressure which has become associated with the aliphatic triazo-esters. Whilst the effervescence brought about by stannous chloride in hydrochloric acid is very vigorous, that induced by concentrated sulphuric acid is very slow. A distinction from the lower homologue is offered by the behaviour towards concentrated potassium hydroxide, because on heating the ester with excess of this agent, violent liberation of nitrogen sets in, followed by ammonia, and, on cooling the liquid, there separate crystals of potassium propionyl-formate, containing 28.2 per cent. of potassium ($C_4H_5O_3K$ requires $K = 27.9$ per cent.); the phenylhydrazone was prepared, and melted at 148.5° after crystallisation from dilute alcohol.

Ethyltriazomalonamide, $C_2H_5 \cdot CN_3(CO \cdot NH_2)_2$.

The substance was obtained by shaking the ester with concentrated aqueous ammonia, and crystallised from hot benzene in colourless, rhombic plates melting at 167° :

0.1027 gave 36.8 c.c. N_2 at 20° and 763 mm. $N = 41.05$.

$C_5H_9O_2N_5$ requires $N = 40.93$ per cent.

Decomposition with stannous chloride in hydrochloric acid readily gave the calculated amount of nitrogen, but the remarkable behaviour of the lower homologue towards concentrated sulphuric acid was reproduced by ethyltriazomalonamide, which was not decomposed below 125° .

Phenyltriazomalonic Acid, $C_6H_5 \cdot CN_3(CO_2H)_2$.

As appears below, it was not found possible to distil phenyltriazomalonic ester, even under pressure reduced to 0.56 mm., without decomposition, which took place at 150° , and accordingly the undistilled material was employed as the source of the acid. Several grams of the ester were shaken with the calculated amount of potassium hydroxide in the form of a 20 per cent. aqueous solution until, in the course of about three hours, a clear liquid resulted; this was extracted twice with ether, acidified with the calculated amount of dilute sulphuric acid, saturated with solid ammonium sulphate, and further extracted five times with ether. After drying with ignited sodium sulphate, the residue from evaporation was submitted to diminished pressure (20 mm.) during thirty-four hours, when it solidified and became colourless on porous earthenware. Recrystallisation from hot benzene gave spherical clusters of snow-white needles melting at 99° without decomposition:

0.1562 gave 25.8 c.c. N_2 at 18° and 768 mm. $N = 19.28$.

$C_9H_7O_4N_3$ requires $N = 19.00$ per cent.

Phenyltriazomalonic acid effervesces vigorously with concentrated sulphuric acid, while torrents of nitrogen are liberated by a solution of stannous chloride in hydrochloric acid; 40 per cent. aqueous potassium hydroxide effects immediate disruption of the triazo-group in the cold, but alkali of half this concentration requires to be heated before bringing about decomposition, when ammonia and nitrogen are liberated without formation of hydrazoic and hydrocyanic acids. The alkaline liquid from the foregoing experiment gave an immediate precipitate with phenylhydrazine after being neutralised with dilute sulphuric acid; this was found to be identical with the phenylhydrazone of benzoylformic acid obtained by similar procedure from phenyltriazooacetic acid, whence it follows that the disruption of the triazo-group is preceded by removal of carbon dioxide from the dibasic acid.

Ethyl Phenyltriazomalonate, $C_6H_5 \cdot CN_3(CO_2 \cdot C_2H_5)_2$.

Phenylmalonic ethyl ester was prepared according to the method of Wislicenus (*Ber.*, 1894, **27**, 1093; *Annalen*, 1888, **246**, 315), which depends on elimination of carbon monoxide from phenyloxalic ester obtained by the action of ethyl oxalate on the sodium derivative of ethyl phenylacetate. Wislicenus states that ethyl phenylmalonate tends to decompose when boiled under atmospheric pressure at 285° , and therefore distilled it at $170\text{--}172^\circ/14$ mm.; our specimen boiled at $127\text{--}129^\circ/0.35\text{--}0.4$ mm. The bromination of phenylmalonic ester has been described by Wheeler and Johnson (*J. Amer. Chem. Soc.*, 1902, **24**, 680), who carried out this operation in sealed tubes, but we find that phenylbromomalonic ester may be prepared in almost quantitative yield by heating the ester with the halogen under ordinary pressure at $140\text{--}150^\circ$ in bright daylight, the product distilling at $141\text{--}142^\circ/0.48$ mm.

Phenylbromomalonic ester (18.5 grams), sodium azide (6 grams), and alcohol (10 c.c.), with sufficient water to maintain the salt dissolved, were left in darkness during three weeks with frequent shaking and occasional warming to about 40° ; water was then added, and the precipitated ester extracted and dried, but an attempt to distil the product was fruitless, owing to the decomposition which was threatened on raising the temperature of the bath to 150° , when the pressure rose from 0.56 mm. to 1.5 mm. quite suddenly, and the operation was therefore discontinued. There was not any indication of distillation taking place, and it has not been possible, therefore, to obtain the substance in purified condition.

The crude ester is a slightly yellow, heavy oil with a faint, pleasant perfume; the decomposition with concentrated sulphuric acid takes

place readily, and nitrogen is liberated also by a solution of stannous chloride in hydrochloric acid. The action of potassium hydroxide has been already described.

Phenyltriazomalonamide, $C_6H_5 \cdot CN_3(CO \cdot NH_2)_2$.

On continued shaking with strong aqueous ammonia, phenyltriazomalonamic ester was transformed into a crystalline solid, which dissolved in hot water, and separated therefrom in snow-white, fern-like leaflets; the substance melted at 189° :

0.1038 gave 29.7 c.c. N_2 at 23° and 760 mm. $N = 32.24$.

$C_9H_9O_2N_5$ requires $N = 31.96$ per cent.

Phenyltriazomalonamide is moderately soluble in acetone, ethyl acetate, and ethyl alcohol; it dissolves sparingly in boiling benzene, and is insoluble in boiling petroleum.

The action of concentrated sulphuric acid on the amide is mild at first, and becomes brisk only on continued stirring, whilst a solution of stannous chloride in hydrochloric acid does not liberate nitrogen until a few drops of alcohol have been added to complete contact. When heated with 20 per cent. aqueous potassium hydroxide, the compound evolves nitrogen freely, accompanied by ammonia, the odour of phenylcarbylamine being also noticeable; hydrazoic and prussic acids, however, were not produced.

Ethyl Bistriazomalonate, $(N_3)_2C(CO_2 \cdot C_2H_5)_2$.

Ethyl dichloromalonamic ester was obtained as a by-product in the preparation of ethyl chloromalonamic ester on treating malonic ester with chlorine at 80° , and boiled at $231\text{--}234^\circ$. It is noteworthy that, although ethyl dichloromalonate may be preserved during many months without showing any signs of having undergone change, the monochloro-compound (b. p. $222\text{--}223^\circ$) became transformed into a brownish-grey, fuming liquid, having a marked odour of hydrogen chloride.

Twenty grams of rectified dichloromalonamic ester, 20 c.c. of absolute alcohol, and 14 grams of sodium azide dissolved in 40 c.c. of water were warmed carefully until the liquid became clear, and left in darkness during one month, with occasional shaking and gentle warming. On diluting with water and extracting with ether, a colourless oil was obtained, half a gram of which was heated in an open tube under atmospheric pressure before submitting the whole specimen to distillation; no change was observed to take place while the temperature remained below 175° , but at the moment of reaching 180° an explosion of very considerable violence occurred. The main quantity of ester

was then distilled under 0·81 mm. pressure, boiling steadily at 115—115·5°:

0·1576 gave 47·6 c.c. N_2 at 21° and 764 mm. $N = 34·57$.

$C_7H_{10}O_4N_6$ requires $N = 34·71$ per cent.

Bistriazomalonic ester is a colourless oil with a pleasant perfume; it has sp. gr. 1·2136 at 20° compared with water at the same temperature. The decomposition by concentrated sulphuric acid is extremely violent, and the liberation of nitrogen with stannous chloride in hydrochloric acid torrential:

0·3251 gave with $SnCl_2$ 62·6 c.c. N_2 at 21° and 768 mm. $N = 22·3$.

0·1816 „ „ H_2SO_4 36·2 c.c. N_2 „ 21° „ 764 mm. $N = 22·8$.

$C_7H_{10}O_4N_6$ requires $2/3N = 23·14$ per cent.

An attempt to prepare bistriazomalonic acid by hydrolysing the ester with 10 per cent. alkali was unsuccessful, owing to the readiness with which the product undergoes spontaneous loss of hydrazoic acid. Seven grams were shaken with the calculated amount of the agent until dissolved, extracted with ether, and treated with the exact quantity of dilute sulphuric acid, after which ammonium sulphate was added and the bistriazomalonic acid removed by four extractions with ether. The solvent having been evaporated without heating, it was noticed that the residual oil, which remained viscous, acquired a distinct odour of hydrazoic acid, and was filled with bubbles which ceased to appear after many days in the desiccator:

0·1410 gave 43·4 c.c. N_2 at 23° and 757 mm. $N = 34·6$.

$C_3H_2O_4N_6$ requires $N = 45·16$ per cent.

$C_2H_3O_3N_3$ „ „ $N = 35·8$ „ „

The latter formula represents triazoglycollic acid, which is very likely produced by the removal of carbon dioxide and hydrazoic acid from bistriazomalonic acid under the influence of water. After many days, crystals of oxalic acid were noticed in the oil, which was treated with a paste of barium carbonate in order to isolate, if possible, barium triazoglycollate. The aqueous filtrate from barium oxalate and unchanged barium carbonate was evaporated to dryness without heat, and triturated with absolute alcohol, the insoluble portion being then analysed:

0·0786 gave 0·0498 $BaSO_4$. $Ba = 37·25$.

$C_4H_4O_6N_6$ Ba requires $Ba = 37·13$ per cent.

The substance effervesced vigorously with concentrated sulphuric acid, and was most probably barium triazoglycollate.

Bistriazomalonamide, $(\text{N}_3)_2\text{C}(\text{CO}\cdot\text{NH}_2)_2$.

Agitation with strong aqueous ammonia during one hour transformed bistriazomalonic ester into a snow-white, crystalline solid, which was recrystallised from boiling water, being only very sparingly soluble therein; the amide separated in transparent, colourless prisms, melting at 162° with vigorous decomposition:

0.0866 gave 47.6 c.c. N_2 at 24° and 765 mm. $\text{N} = 60.88$.

$\text{C}_3\text{H}_4\text{O}_2\text{N}_8$ requires $\text{N} = 60.89$ per cent.

The substance is readily soluble in hot acetone and ethyl acetate, crystallising therefrom in six-sided plates; it is moderately soluble in cold alcohol, but dissolves very sparingly in boiling benzene and in boiling chloroform. Immediate effervescence occurs on mixing the amide with concentrated sulphuric acid, and becomes very vigorous on warming; stannous chloride also liberates nitrogen very freely. The decomposition with 40 per cent. potassium hydroxide is most profound, giving rise to nitrogen, ammonia, prussic acid, and hydrazoic acid.

Phenyltriazooacetic Acid, $\text{C}_6\text{H}_5\cdot\text{CHN}_3\cdot\text{CO}_2\text{H}$.

Owing to the readiness with which the triazo-group in phenyltriazooacetic ester undergoes disruption in the presence of alkali, the acid cannot be obtained by hydrolysis. Five grams of phenylchloroacetic acid were therefore exactly neutralised with sodium carbonate in about 30 c.c. of water, and, after admixture with 2.5 grams of sodium azide dissolved in 20 c.c. of water, allowed to remain during two days protected from light; dilute sulphuric acid having been added, and the liquid extracted six times with ether, the latter was dried with sodium sulphate and evaporated in a vacuum desiccator without being heated. The residue became solid, and was recrystallised three times from benzene, which deposited the substance in thin, colourless, rhombic plates melting at 98.5° :

0.1543 gave 31.4 c.c. N_2 at 20° and 764 mm. $\text{N} = 23.41$.

$\text{C}_8\text{H}_7\text{O}_2\text{N}_3$ requires $\text{N} = 23.73$ per cent.

The decomposition with concentrated sulphuric acid was very violent, and nitrogen was also liberated immediately on mixing the acid with aqueous potassium hydroxide or a solution of stannous chloride in hydrochloric acid. The silver salt could not be analysed, because reduction took place on attempting to recrystallise it from warm water.

Ethyl Phenyltriazooacetate, $\text{C}_6\text{H}_5\cdot\text{CHN}_3\cdot\text{CO}_2\cdot\text{C}_2\text{H}_5$.

Early attempts to prepare this ester were conducted on the lines followed in the case of triazoacetic ester and its higher homologues,

but the results were unsatisfactory; when alcoholic phenylchloroacetic ester is heated under reflux with aqueous sodium azide, the liquid rapidly becomes yellow and evolves gas, and, although the oily product of steam distillation answers to the azide test with concentrated sulphuric acid, it is too complex a mixture to repay further treatment, the presence of by-products being best avoided by the following procedure.

Eighty grams of phenylchloroacetic ester (b. p. $135^{\circ}/17$ mm.) were mixed with 100 grams of alcohol and 40 grams of sodium azide (1 mol. = 26.2 grams), water and alcohol being then added alternately until both ester and salt were dissolved; after remaining a few weeks in the dark, the liquid was found to have deposited a crop of sodium chloride, and at the end of two months, when the action was judged to have been complete, water and solid ammonium sulphate were added to precipitate the ester, which was then removed, dried in the usual way, and fractionated with the aid of the Gaede pump:

0.2204 gave 38.3 c.c. N_2 at 16° and 770 mm. $N = 20.08$.

$C_{10}H_{11}O_2N_3$ requires $N = 20.49$ per cent.

Ethyl phenyltriazooacetate is a colourless liquid with a very faint pleasant perfume suggesting roses; only on distilling the ester with steam does the vapour produce the throbbing sensation at the base of the forehead and palpitation of the heart characteristic of the aliphatic triazo-esters. It boils at $93^{\circ}/0.09$ mm., and has sp. gr. 1.1434 at $20^{\circ}/20^{\circ}$; the action with concentrated sulphuric acid is very violent.

Action of Potassium Hydroxide.—Contact with dilute aqueous alkali was found to bring about an immediate disruption of the triazo-group, and it was therefore useless to attempt hydrolysis by this means. On adding 40 per cent. potassium hydroxide drop by drop to 10 grams of the ester dissolved in 40 c.c. of alcohol, the liberation of nitrogen was perfectly regular, and, after excess of alkali had been added, there separated a reddish oil which in the vacuum-desiccator rapidly solidified; this product, being sparingly soluble in water, was recrystallised from the gently warmed liquid, and was obtained in colourless, nacreous plates:

0.3114 gave 0.1470 K_2SO_4 . $K = 21.16$.

0.2577 „ 16.7 c.c. N_2 at 19° and 768 mm. $N = 7.53$.

$C_8H_6O_2NK$ requires $K = 20.85$; $N = 7.49$ per cent.

In the course of twenty-four hours' exposure to air, the substance had begun to undergo hydrolysis, yielding potassium benzoylformate, and when the salt no longer contained nitrogen, benzoylformic acid was obtained from it and identified by the melting point (65°) and by conversion into the phenylhydrazone, a specimen of which melted at

160° and contained 11·8 per cent. of nitrogen ($C_{14}H_{12}O_2N_2$ requires $N = 11·7$ per cent.).

Action of Ammonia.—Attempts to prepare phenyltriazacetamide by the action of ammonia on phenyltriazacetate were unsuccessful, owing to disruption of the triazo-group; this can, however, be so controlled as to permit the isolation of *phenyliminoacetamide*. Excess of dry ammonia was passed into a well-cooled solution of phenyltriazacetate in absolute alcohol; liberation of nitrogen accompanied the separation of crystals, which increased during twenty-four hours in the ice-chest. Recrystallisation from benzene, repeated until the melting point was constant, gave colourless, monoclinic plates melting at 144°:

0·2070 gave 34·3 c.c. N_2 at 20° and 770 mm. $N = 19·21$.

$C_8H_8ON_2$ requires $N = 18·92$ per cent.

The substance is readily soluble in alcohol and in benzene, being precipitated from the respective solutions by water and by petroleum. When exposed to air it produces ammonia, giving the α -amide of benzoylformic acid, m. p. 90°. The acid itself was obtained by completing the hydrolysis.

Triazacetophenone (Phenacylazoimide), $N_3 \cdot CH_2 \cdot CO \cdot C_6H_5$.

Twenty grams of bromoacetophenone dissolved in 50 c.c. of absolute alcohol and mixed with 7 grams of sodium azide in the minimum quantity of water were shaken at intervals during sixteen hours in the ice-chest; being very readily fusible, the crystalline product was collected on a filter, cooled with chilled brine, and then precipitated by petroleum from a dried ethereal solution:

0·1695 gave 38·4 c.c. N_2 at 20° and 767 mm. $N = 26·16$.

$C_8H_7ON_3$ requires $N = 26·09$ per cent.

The triazoketone crystallises in colourless, lustrous plates, and melts at 17°; in the course of a few weeks the pale yellow substance became dark brown, even when protected from light, and the odour of hydrazoic acid was perceptible. An attempt to distil it under 0·1 mm. pressure was unsuccessful, because a threatening decomposition set in when the temperature of the bath had reached 130°, the pressure quickly rising to 4 mm.

On adding 20 per cent. potassium hydroxide to an alcoholic solution of triazacetophenone, immediate liberation of nitrogen takes place followed by ammonia on heating the liquid; a deep red coloration is developed, but the indication of hydrazoic acid is trifling. An attempt to establish the intermediate production of benzoylformaldehyde on the lines indicated by W. L. Evans (*J. Amer. Chem. Soc.*, 1906, **34**, 115) was unsuccessful, the only material isolated being

benzoic acid. Two grams in ether were shaken with one gram of lime and 40 c.c. of water, the mixture liberating gas immediately and becoming dark brownish-red; after thirty hours the aqueous liquid was removed, extracted three times with ether, and acidified, when further extraction removed benzoic, not mandelic, acid.

Phenacylazoimide reduces ammoniacal silver oxide in the cold solution.

Action of Sulphuric Acid.—The concentrated agent attacks the triazoketone with great violence, and flame sometimes accompanies the small explosion which occurs when they are mixed drop by drop. By using more dilute acid the action can be moderated, until at 25 per cent. the yield of nitrogen may be measured:

0.2336 gave 34.4 c.c. N_2 at 18° and 772 mm. $N = 17.27$.

$C_8H_7ON_3$ requires $2/3N = 17.39$ per cent.

To complete the decomposition it was found necessary to use a bath of hot brine, and on cooling the contents of the flask, crystals of benzoic acid separated.

Behaviour towards Stannous Chloride.—With a cold 20 per cent. solution of the metal in hydrochloric acid the decomposition was very slow, and, even after heating during two hours, the quantity of gas was deficient:

0.1586 gave 22.9 c.c. N_2 at 18° and 772 mm. $N = 16.95$.

$C_8H_7ON_3$ requires $2/3N = 17.39$ per cent.

The aromatic product was not identified.

The Semicarbazone.—An alcoholic solution of the triazoketone was mixed with aqueous semicarbazide acetate, the solid which separated during twelve hours being recrystallised from warm dilute alcohol:

0.0895 gave 29.6 c.c. N_2 at 19° and 773 mm. $N = 38.68$.

$C_9H_{10}ON_6$ requires $N = 38.52$ per cent.

The substance crystallised in colourless, silky needles, melting at 127.5 — 128.5° . The reaction with concentrated sulphuric acid was very vigorous.

The Bromophenylhydrazone.—The derivative crystallised from dilute alcohol in lustrous, yellow needles, melting at 114.5° :

0.1079 gave 20.1 c.c. N_2 at 19° and 768 mm. $N = 21.64$.

$C_{14}H_{12}N_5Br$ requires $N = 21.21$ per cent.

Triazoacetophenoneoxime, $N_3 \cdot CH_2 \cdot C(:NOH) \cdot C_6H_5$.

Triazoacetophenone was suspended in an aqueous solution of hydroxylamine prepared by exactly neutralising with sodium carbonate a slight excess of the hydrochloride; alcohol was then added until, with gentle warming, a clear solution was produced. After three

days in the dark, a pale yellow oil had separated, and this, after adding water, was extracted with ether, dried with sodium sulphate, and freed from solvent in the vacuum desiccator. As in the case of triazoacetone (Trans., 1908, 93, 84), it was not found possible to crystallise the oxime, which was therefore analysed in liquid form:

0.1050 gave 28.4 c.c. N_2 at 18° and 771 mm. $N = 31.70$.

$C_8H_8ON_4$ requires $N = 31.82$ per cent.

An attempt to produce the *p*-toluenesulphonyl derivative, which served to characterise triazoacetoxime (*loc. cit.*), led to an uninviting black tar.

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XVI.—Organic Derivatives of Silicon. Part XII.*

Dibenzylethylpropylsilicane and Sulphonic Acids Derived from It.

By FREDERICK CHALLENGER, B.Sc., and FREDERIC STANLEY KIPPING.

WHEN the study of organic derivatives of silicon was commenced by one of us, the principal object in view was the preparation of an optically active compound containing *one* asymmetric silicon group.

After a short experience of the behaviour of silicon derivatives, the plan which seemed to offer the best prospect of success was to synthesise some asymmetric silico-hydrocarbon, $SiR_1R_2R_3R_4$, which could afterwards be sulphonated, and then to resolve the *dl*-sulphonic acid which would be thus obtained.

In pursuance of this plan, phenylmethylethylpropylsilicane, $SiPhMeEtPr$, and phenylbenzylethylpropylsilicane, $SiPhEtPr \cdot CH_2Ph$, were first prepared; but on attempting to sulphonate these compounds, the phenyl group was eliminated as benzene and tertiary silicols were formed (Kipping, Trans., 1907, 91, 221).

In the case of the phenylbenzyl derivative, this unexpected behaviour did not necessitate any change in the original scheme, as it was found that a sulphonic acid could be obtained from the benzylethylpropylsilicol, $CH_2Ph \cdot SiEtPr \cdot OH$, which was produced from the silico-hydrocarbon.

Further investigation showed, however, that this sulphonic acid was derived from the oxide, $(SiEtPr \cdot CH_2Ph)_2O$, and therefore contained *two* asymmetric silicon groups; this fact, of course, upset the original

* Parts X and XI, Trans., 1909, 95, 302 and 489 respectively.

plan, but at the same time opened out an alternative one, for if the *dl*-sulphonic derivative of benzylethylpropylsilicyl oxide which was thus obtained proved to be the *dl*- and not the internally compensated compound, it might be resolved into its optically active components. These possibilities were ultimately realised, and in later investigations the resolution of the homologous sulphonic acid derived from benzylethylisobutylsilicyl oxide, $(C_4H_9 \cdot SiEt \cdot CH_2Ph)_2O$, was also accomplished (Kipping, *Trans.*, 1907, **91**, 234; Luff and Kipping, *Trans.*, 1908, **93**, 2090).

These acids, which owe their optical activity to the presence of *two* asymmetric silicon groups, are the only active silicon compounds which so far have been described; they hold this position, not because the original object has been abandoned, but because all attempts to attain it resulted in failure.

Thus, during the progress of the experiments referred to above, two other asymmetric silico-hydrocarbons, namely, benzylmethylethylpropylsilicane, $SiMeEtPr \cdot CH_2Ph$, and benzylethylpropylisobutylsilicane, $C_4H_9 \cdot SiEtPr \cdot CH_2Ph$ (Kipping, *Trans.*, 1907, **91**, 717; Kipping and Davies, *Trans.*, 1909, **95**, 69), were prepared and sulphonated, and many attempts were made to resolve the *dl*-acids thus produced. Although, however, the externally compensated character of the acids could hardly be open to question, no definite evidence of their asymmetry was obtained on fractionally crystallising their salts with active bases.

Our knowledge of asymmetric substances is still so incomplete that a reason for these repeated failures can hardly be suggested with any confidence. It seemed possible, however, that by preparing a compound in which the groups combined with the silicon atom were more widely different than those in the two acids under discussion, the chances of being able to accomplish a resolution would be increased.

Now as most of the readily available alkyl and aryl halogen compounds had already been utilised in the preparation of the four asymmetric silico-hydrocarbons referred to above, the simplest way of obtaining a new asymmetric sulphonic acid of the desired character seemed to be to prepare a silico-hydrocarbon containing two benzyl groups and two different alkyl groups, and then to convert this compound into an asymmetric acid by sulphonating one of the benzyl groups.

The present paper contains a record of the experiments which have led to the production of such an acid, namely, dibenzylethylpropylsilicanemonosulphonic acid, $CH_2Ph \cdot SiEtPr \cdot CH_2 \cdot C_6H_4 \cdot SO_3H$; the disulphonic acid, $SiEtPr(CH_2 \cdot C_6H_4 \cdot SO_3H)_2$, derived from the same silico-hydrocarbon has also been obtained.

Dibenzylethylpropylsilicane, $SiEtPr(CH_2Ph)_2$, was prepared by the

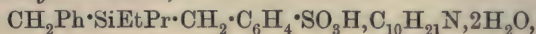
interaction of benzylethylpropylsiliclyl chloride (Kipping, Trans., 1907, 91, 722) and magnesium benzyl chloride; a simpler method, which was afterwards adopted, consisted in preparing dibenzylethylsiliclyl chloride directly from ethylsilicon trichloride and then treating this product with magnesium propyl bromide.

The compound thus obtained, like all those silico-hydrocarbons which contain a benzyl group, is readily attacked by chlorosulphonic acid at the ordinary temperature, and under suitable conditions it yields a monosulphonic acid, which, however, is invariably accompanied by a disulphonic acid. It would seem that in both cases only one of the possible structural isomerides is formed in appreciable quantities, namely, the para-derivative.

The isolation of these two sulphonic acids was by no means a simple task, but it was at last accomplished by two methods, namely, by fractionally crystallising the mixture of strychnine salts, or of *l*-menthylamine salts, prepared from the product of sulphonation. The disulphonic acid, which has the symmetrical constitution given above, and is consequently of little interest, has not been examined much further than was necessary for establishing its composition. Its *strychnine* salt is more soluble in water than the salt of the monosulphonic acid, and decomposes from about 226°. Its *l*-menthylamine salt is practically insoluble in light petroleum, and melts at 205—208°. The ammonium, sodium, and barium salts are crystalline.

The *strychnine* and the *l*-menthylamine salts of the *dl*-monosulphonic acid are not resolved during the prolonged course of fractional crystallisation which is necessary in separating them from the derivatives of the disulphonic acid. The *strychnine* salt crystallises well, and melts at 199°.

The *l*-menthylamine salt,



crystallises from moist light petroleum in lustrous plates, and is very similar in properties to the corresponding salts of the monosulphonic derivatives of benzylmethylethylpropylsilicane and benzylethylpropylisobutylsilicane. This fact was by no means promising, and seemed to indicate that attempts to resolve the new *dl*-acid would be just as unsuccessful as those already recorded in the case of the acids just mentioned. Fortunately, however, the great uncertainty of conclusions based on analogy in dealing with asymmetric compounds was again illustrated, as, after a few failures, the acid was easily resolved into its optically active components.

An account of the resolution experiments and of the properties of the active acids will be given in the near future.

EXPERIMENTAL.

Preparation of Dibenzylethylsilicyl Chloride, $\text{SiEtCl}(\text{CH}_2\text{Ph})_2$.

Ethylsilicon trichloride (1 mol., 250 grams), diluted with about six times its volume of dry ether, and magnesium powder (1 atom) are placed together in a large flask, which is provided with a tap-funnel, a stirrer, and a suitable outlet tube.

A little benzyl chloride (2—3 c.c.) and a small quantity of an ethereal solution of magnesium benzyl chloride (prepared in a test-tube) are now added, and the flask is gently warmed. In a short time a reaction sets in, accompanied by the separation of magnesium chloride, and, as soon as this reaction becomes fairly vigorous, the flask is immersed in melting ice and the stirrer is started. Benzyl chloride (2 mols.) is then run in drop by drop, an operation which occupies about two and a-half hours; when the whole of it has been added, the contents of the flask are heated under a reflux condenser during three to four hours. After cooling the product, the granular precipitate of magnesium chloride is separated by filtration in absence of moisture (compare Kipping, Trans., 1907, 91, 216) and is washed several times with dry ether; on evaporating the combined ethereal filtrate and washings, there remains a yellow liquid, which fumes in moist air.

This liquid is first roughly fractionated under 100 mm. pressure from an ordinary distillation flask. Very little passes over below 165° , but between this temperature and 210° a fairly large fraction is collected. The thermometer then rises quickly to 238° , and another large fraction distils from 238° to 290° . Distillation may be continued up to 320° , or even higher, but this fraction has been only superficially examined; the dark green liquid which then remains in the flask is sometimes pasty, owing to the presence of magnesium chloride.

By systematically fractionating the liquid boiling between 165° and 210° , using a long-necked flask with a rod-and-disk column, benzylethylsilicon dichloride (Kipping, Trans., 1907, 91, 720) is obtained as an oil boiling at $168\text{--}170^\circ/100$ mm. The rest of the original distillate when similarly fractionated yields a liquid passing over between 246° and $251^\circ/70$ mm., almost the whole of which, however, boils constantly at 249° . The yield of this product is 40—50 per cent. of the theoretical. The fractions boiling at about $300^\circ/40$ mm. contain a small quantity of tribenzylsilicyl chloride which separates in crystals on cooling. The formation of this substance is probably due to the presence of silicon tetrachloride in the ethylsilicon trichloride which was employed, and not to the displacement of an ethyl by a benzyl group; from a longer experience of silicon compounds it is concluded that such displacements, at one time thought to be possible (Robison and Kipping, Trans., 1908, 93, 440), do not occur.

The liquid boiling at $249^{\circ}/70$ mm. consists of dibenzylethylsilicyl chloride. It was analysed by decomposing it with dilute ammonia and titrating the neutral solution with silver nitrate ; 1 c.c. = 0.003509 gram Cl (Kipping, Trans., 1907, 91, 217) :

0.9788 required 35.9 c.c. AgNO_3 . Cl = 12.8.

$\text{C}_{16}\text{H}_{19}\text{ClSi}$ requires Cl = 12.9 per cent.

Dibenzylethylsilicyl chloride is an almost colourless oil, possessing, especially when freshly distilled, a fine bluish-violet fluorescence, which is probably due to traces of impurity. It has an aromatic, pungent odour, fumes in moist air, and is rapidly decomposed by water, giving dibenzylethylsilicol, which passes spontaneously into dibenzylethylsilicyl oxide (m. p. 56°) when it is kept over sulphuric acid for a week or two.

Dibenzylethylpropylsilicane, $\text{SiEtPr}(\text{CH}_2\text{Ph})_2$.

Dibenzylethylsilicyl chloride (1 mol., 170 grams) is mixed with an ethereal solution of magnesium propyl bromide ($1\frac{1}{10}$ mols.), and the ether is distilled off. Very little, if any, action takes place until most of the ether is removed, when a slight separation of magnesium chlorobromide is observed. The mixture is then heated for about two hours at 140 — 180° , at the end of which time it is cooled and treated with water. The oil which separates is extracted with ether and fractionated under 90 mm. pressure.

Distillation begins at about 250° , the thermometer quickly rising to 262° . Most of the product then passes over between 262° and 270° , and only a small quantity of high boiling residue remains in the flask. After further fractionation, pure dibenzylethylpropylsilicane, boiling at 262 — $265^{\circ}/90$ mm., is obtained. The yield is 70 to 80 per cent. of the theoretical :

0.1417 gave 0.4166 CO_2 and 0.1181 H_2O . C = 80.17 ; H = 9.24.

(A)* 0.2244 gave 0.0464 SiO_2 . Si = 9.7.

(B) 0.1202 „ 0.0253 SiO_2 . Si = 9.89.

$\text{C}_{19}\text{H}_{26}\text{Si}$ requires C = 80.68 ; H = 9.2 ; Si = 10.05 per cent.

The first samples of dibenzylethylpropylsilicane were prepared by the interaction of benzylethylpropylsilicyl chloride and magnesium benzyl chloride. Benzylethylpropylsilicyl chloride (1 mol., 20 grams) is added to an ethereal solution of magnesium benzyl chloride ($1\frac{1}{5}$ mols.), and, as no sign of a reaction occurs at this stage, the ether is distilled off and the residue is heated at about 140° during one to two hours. The pasty mass of oil and magnesium chloride is cooled and treated with water, and the oil extracted with ether.

When the crude product is distilled under 100 mm. pressure, it

* A and B were different preparations.

begins to boil at about 210° , and from this temperature to 240° a little dibenzyl passes over; the thermometer then rises rapidly to 260° , and the silico-hydrocarbon begins to distil. From the liquid collected between 260° and 280° , dibenzylethylpropylsilicane is obtained by further fractional distillation:

0.1948 gave 0.5790 CO_2 and 0.1628 H_2O . $\text{C} = 81.06$; $\text{H} = 9.3$.

0.4567 „ 0.0945 SiO_2 . $\text{Si} = 9.73$.

$\text{C}_{19}\text{H}_{28}\text{Si}$ requires $\text{C} = 80.68$; $\text{H} = 9.2$; $\text{Si} = 10.05$ per cent.

Although the yield by this method was very satisfactory, the task of preparing benzylethylpropylsilicyl chloride, even in an approximately pure condition, is far more troublesome than that of preparing pure dibenzylethylsilicyl chloride; for this reason, practically the whole of the silicane used in this investigation was obtained by the method described on p. 146.

Dibenzylethylpropylsilicane is a colourless liquid with a beautiful violet fluorescence. It has a pleasant aromatic odour, and is lighter than water. It is miscible with most organic solvents.

Sulphonation of Dibenzylethylpropylsilicane.

Knowing from previous experience (Kipping, Trans., 1907, 91, 223) that sulphuric acid is not a satisfactory sulphonating agent in the case of the silico-hydrocarbons, chlorosulphonic acid was used in the sulphonation of dibenzylethylpropylsilicane, and, as it seemed very likely that both benzyl groups might be attacked, chlorosulphonic acid ($1\frac{1}{2}$ mols.), dissolved in a large volume of chloroform, was gradually added to the well-cooled silicon compound, also in chloroform solution. When nearly two-thirds of this solution had been run in, a test portion of the product was poured into water and the chloroform was boiled off; repeating this test at intervals during the addition of the chlorosulphonic acid, the aqueous solutions of the product gradually altered in character. At first they contained visible drops of unchanged silico-hydrocarbon; later on, however, they were clear and apparently free from oil while hot, but became white and opaque when cooled, or they were white and opaque when hot but became quite clear on cooling.

Thinking that solubility in water was sufficient evidence that sulphonation was complete, and as it was very important not to use too large a quantity of chlorosulphonic acid, the addition of this reagent was generally stopped as soon as a sample of the product gave a clear solution in hot or cold water. Further investigation showed, however, that this test was not trustworthy, and that even when the sulphonation product gave a perfectly clear solution in water (after removing the chloroform by steam distillation), the

solution might nevertheless contain considerable quantities of unchanged silico-hydrocarbon; it was also found that when even the theoretical quantity (1 mol.) of chlorosulphonic acid was employed, a considerable quantity of disulphonic acid was formed.

In these circumstances various proportions of chlorosulphonic acid were tried, and the following method of preparation was finally adopted.

A solution of the hydrocarbon (b. p. 262—266°/90 mm.) in chloroform (6 vols.) is cooled in ice, and a solution of chlorosulphonic acid ($1\frac{1}{2}$ mols.) in chloroform (12 vols.) is added to it drop by drop while a rapid stream of dry carbon dioxide is passed through the mixture. Hydrogen chloride is evolved almost immediately, and the liquid soon assumes a red colour, which darkens slightly as the process continues.

After keeping the mixture at 0° for a short time, it is poured on ice, and, from the very slowly settling emulsion thus obtained, the chloroform is separated by steam distillation.

If the distillation is continued after all the chloroform has been removed, oil continues to pass over in small quantities during two or three hours. This oil is more quickly separated by extracting with ether; it consists almost entirely of unchanged dibenzylethylpropylsilicane, but sometimes contains relatively very small quantities of dibenzylethylsilicyl oxide (m. p. 56°), a fact which seems to show that the not very highly purified samples of the silico-hydrocarbon used in the preparation of the sulphonic acid contained small quantities of dibenzylethylsilicol.

The almost colourless aqueous solution of the sulphonic acid, which has been exhaustively extracted with ether, does not show the peculiar behaviour referred to above, which, therefore, must be attributed to the presence of the silicane. It is very remarkable, however, that the silicane should dissolve in an aqueous solution of the sulphonic acid.

Isolation of the Sulphonic Acids.

Many difficulties were met with in attempting to isolate the sulphonic acids produced in the manner described above. The ammonium salt was first prepared and freed from mineral salts by the method previously used in other cases (Kipping, Trans., 1907, 91, 225), but the crude salt was a syrupy or pasty substance, and could not be obtained in crystals. From the crude ammonium salt, many salts of organic bases were obtained by precipitation; of these, the strychnine salt alone gave crystalline deposits from suitable solvents, and consequently this base was first employed for the purpose in view.

In later experiments, when the properties of the sulphonic acids were known, *l*-menthylamine was used instead of strychnine, but as there is little to choose between the two methods, they are both described.

Method I.—The aqueous solution of the product of sulphonation is neutralised with sodium carbonate and treated with a concentrated solution of strychnine hydrochloride. The precipitate which is first produced dissolves on stirring, and, after some time, the solution acquires the appearance of raw white of egg, but on adding more strychnine hydrochloride a yellow oil is precipitated. The almost clear supernatant liquid is decanted, and the oil is then stirred with a little more of the solution of strychnine hydrochloride, after which it is extracted five or six times with boiling water and, lastly, with hot 8 per cent. aqueous acetone.

The remaining oil is then dissolved in alcohol, the solution diluted with about half its volume of water, and cooled in ice; the crystalline deposit which is thus obtained is further purified by repeated crystallisation from aqueous alcohol, and finally from anhydrous ethyl acetate containing a trace of acetone. This product is the strychnine salt of *dl*-dibenzylethylpropylsilicanemonosulphonic acid.

The aqueous extracts of the crude strychnine salt, and also those obtained with 8 per cent. aqueous acetone, deposit white, asbestos-like needles, together with a considerable proportion of oil. After separating the crystals by the aid of the pump, the oil is again extracted twice with hot water, by which means a further quantity of the crystalline compound is obtained. The insoluble oily residue then consists principally of the strychnine salt of the monosulphonic acid, and is treated accordingly.

The salt which is soluble in hot water is dissolved in acetone, which contains a very small proportion of water, and the solution is allowed to evaporate spontaneously. The substance which is then deposited, after having been recrystallised from methyl alcohol, consists of the strychnine salt of dibenzylethylpropylsilicanedisulphonic acid.

Method II.—The aqueous solution containing the sodium salts of the sulphonic acids is treated with excess of a solution of *l*-menthylamine hydrochloride, and the precipitated oil is washed with water; this oil is then repeatedly extracted with boiling light petroleum (b. p. 40–60°). From these extracts the crude *l*-menthylamine salt of *dl*-dibenzylethylpropylsilicanemonosulphonic acid is deposited in lustrous plates on cooling and stirring well with a little water. This salt, however, still contains some *l*-menthylamine salt of the disulphonic acid, from which it is separated by repeated recrystallisation from moist light petroleum. In these operations, petroleum of very low boiling point gives the best results, because, although the pure *l*-menthylamine salt of the disulphonic acid is insoluble even in light

petroleum boiling at 60—80°, it dissolves to a considerable extent in presence of the salt of the monosulphonic acid.

That portion of the precipitated oil which is insoluble in light petroleum is dissolved in a small quantity of methyl alcohol, and treated with ethyl acetate until the well-stirred solution becomes very slightly turbid. If kept over sulphuric acid, nodular masses of the *l*-menthylamine salt of dibenzylethylpropylsilicanedisulphonic acid are deposited. From the mother liquors, a further amount of the *l*-menthylamine salt of the *dl*-monosulphonic acid can be obtained by evaporating them and extracting the residue with light petroleum.

Strychnine dl-Dibenzylethylpropylsilicanemonosulphonate.

This salt separates from aqueous alcohol or aqueous acetone in hydrated crystals, which melt below 100° and contain 3 molecules of water :

0.9125 of air-dried salt lost 0.0686 H₂O. H₂O = 7.5.

C₄₀H₄₈O₅N₂SSi, 3H₂O requires H₂O = 7.2 per cent.

When the hydrated salt is dissolved in ethyl acetate it quickly separates again in colourless needles, which still contain water of crystallisation and lose weight at 100°.

When heated, these do not soften until 160°, but resolidify above that temperature, and then melt at 199°, the melting point of the anhydrous salt.

The anhydrous salt was analysed :

0.1592 gave 0.4044 CO₂ and 0.0970 H₂O. C = 69.2 ; H = 6.7.

0.8305 „ 0.0717 SiO₂. Si = 4.06.

C₄₀H₄₈O₅N₂SSi requires C = 68.9 ; H = 6.94 ; Si = 4.09 per cent.

The anhydrous salt is only very slightly soluble in dry ethyl acetate, but dissolves readily in acetone, ethyl or methyl alcohol, chloroform, or toluene. It crystallises in leaflets from benzene, in which, however, it is very soluble. Short, stout, prismatic needles are obtained from a mixture of ethyl acetate and acetone. Light petroleum and ether have no solvent action.

The specific rotation of the anhydrous salt was determined in 98 per cent. methyl-alcoholic solution :

0.8771, made up to 25 c.c., gave, in a 2-dcm. tube, α - 0.58° ; whence $[\alpha]_D$ - 8.26°.

In spite of the fact that the isolation of this strychnine salt is only accomplished after a very laborious series of crystallisations from two solvents, the preparation melting at 199° is not a resolution product of the *dl*-monosulphonic acid, as will be shown later.

Conclusive evidence that the salt is really derived from dibenzyl-

ethylpropylsilicanemonosulphonic acid is afforded by the results of analyses of several other compounds prepared in the course of this investigation.

Strychnine Dibenzylethylpropylsilicanedisulphonate.

The pure preparations of this compound, isolated in the manner already described, consist of a white, gritty powder, which turns brown at 226° and melts completely at 231° , above which temperature it rapidly decomposes.

Under the microscope it is seen to consist of short, rather ill-defined, prismatic needles:

0.1894 gave 0.4559 CO_2 and 0.1170 H_2O . $\text{C} = 65.63$; $\text{H} = 6.86$.

0.1780 „ 0.4293 CO_2 „ 0.1098 H_2O . $\text{C} = 65.78$; $\text{H} = 6.86$.

$\text{C}_{61}\text{H}_{70}\text{O}_{10}\text{N}_4\text{S}_2\text{Si}$ requires $\text{C} = 65.8$; $\text{H} = 6.35$ per cent.

Owing to the slight solubility of the salt in 98 per cent. methyl alcohol, the specific rotation was determined in 90 per cent. methyl-alcoholic solution:

0.6162, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 0.75^{\circ}$; whence $[\alpha]_D - 15.21^{\circ}$.

Although the strychnine salt of the disulphonic acid might be expected to have a higher specific rotation than that ($[\alpha]_D - 8.26^{\circ}$) of the salt of the monosulphonic acid, it seemed probable that the very great observed difference might be due to the different proportions of water in the methyl alcohol employed in determining the two values.

This conclusion was confirmed by determining the specific rotation of strychnine dibenzylethylpropylsilicanedisulphonate in methyl alcohol containing 36 per cent. of water:

0.5298, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 0.95^{\circ}$; whence $[\alpha]_D - 22.4^{\circ}$.

The salt is very sparingly soluble in cold methyl or ethyl alcohol, but is moderately soluble in the hot solvents, and also in boiling water; in ethyl acetate, acetone, benzene, and light petroleum it is practically insoluble, but it dissolves freely in chloroform and in aqueous acetone. The crystals deposited from aqueous solutions melt at about 110° , and are doubtless hydrated, as, when dried at 100° , their melting point rises to $226-231^{\circ}$.

1-Menthylamine dl-Dibenzylethylpropylsilicanemonosulphonate.

This salt crystallises from moist light petroleum in high lustrous plates containing 2 molecules of water of crystallisation. The hydrated salt liquefies at temperatures far below 100° , but when

kept over sulphuric acid it is completely dehydrated, and then melts at 99° :

1.3661 lost $0.0855 \text{ H}_2\text{O}$. $\text{H}_2\text{O} = 6.26$.

$\text{C}_{29}\text{H}_{47}\text{O}_3\text{NSSi}, 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.55$ per cent.

The equivalent of the anhydrous salt was determined by boiling with excess of *N*/50-sodium carbonate and then titrating with hydrochloric acid, using litmus as indicator. This method gave the value 516.4, that required by theory being 517.8.

The molecular weight of the anhydrous salt was determined by the cryoscopic method in benzene solution :

Substance.	Solvent.	<i>E</i> .	M.W.
0.795 gram	17.6 grams	0.12	1875

The calculated value is 517.8.

The molecular weight was also determined by the ebullioscopic method in methyl-alcoholic solution :

Substance.	Solvent.	<i>E</i> .	M.W.
0.089 gram	70.0 grams	0.035	305
0.207 "		0.075	332
0.348 "		0.130	322
0.723 "		0.260	334
1.006 "		0.360	336

These results correspond with those given in benzene and in methyl-alcoholic solutions respectively by the *l*-menthylamine salt of benzyl-methylethylpropylsilicanesulphonic acid (Kipping, *Trans.*, 1907, 91, 737), and as the salt is doubtless highly ionised in the latter solvent, the observed values are such as might have been expected.

The specific rotation of the anhydrous salt was determined in methyl-alcoholic solution :

0.707, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 0.76^{\circ}$; whence $[\alpha]_D - 13.4^{\circ}$.

l-Menthylamine *dl*-dibenzylethylpropylsilicanemonosulphonate is insoluble in water, but dissolves freely in all organic solvents. It may be recrystallised from aqueous alcohol and from aqueous acetone, but by far the most suitable solvent is petroleum of low boiling point ; from this liquid the hydrated salt separates almost completely on cooling, but if the solution is boiled for some time, water is expelled, and the solution of the anhydrous salt does not deposit crystals until it has been stirred with water.

Metallic Salts of dl-Dibenzylethylpropylsilicanemonosulphonic Acid.

The sodium salt was prepared by decomposing the pure *l*-menthylamine salt with a slight excess of sodium carbonate and distilling off the liberated base in steam ; the very great frothing which occurs in

the latter operation may be overcome by dropping alcohol continuously into the liquid.

On neutralising the residue with a few drops of acetic acid and evaporating, a soapy mass separates from the cold concentrated solution, but on adding water again and leaving the solution at the ordinary temperature, the salt is deposited in crystals; it is fairly readily soluble in cold water, and extremely so in alcohol. It is precipitated from its aqueous solution by sodium hydroxide, carbonate, or acetate.

The *ammonium* salt was obtained from the pure strychnine salt as a sticky mass on evaporating its aqueous solution. It is more readily soluble in water than the sodium salt, and its solution froths readily.

The *barium* salt was precipitated in flocculent, oily masses when a solution of the sodium salt was treated with a solution of barium chloride. It is only sparingly soluble in cold water or alcohol, but dissolves fairly readily in warm aqueous alcohol.

1-Menthylamine Dibenzylethylpropylsilicanedisulphonate.

This salt crystallises from a mixture of ethyl acetate and methyl alcohol in nodules, which contain water of crystallisation, but which, when anhydrous, melt at 205—208°.

The anhydrous salt is readily soluble in ethyl and methyl alcohols, but is insoluble in water, acetone, ethyl acetate, light petroleum, or benzene.

Metallic Salts of the Disulphonic Acid.

The *ammonium* salt of the disulphonic acid was prepared by treating a warm alcoholic solution of the strychnine salt with excess of ammonium hydroxide; on evaporation of the filtered solution it remained as a yellow solid, which was purified by recrystallisation from a mixture of ethyl acetate and methyl alcohol. It was thus obtained in lustrous plates, readily soluble in the common alcohols and in cold water, but insoluble in ethyl acetate, acetone, or light petroleum.

The equivalent of the compound was determined by boiling the salt with excess of *N*/50-sodium carbonate, and then titrating the solution with acid. The results obtained were 239.4 and 237.4, the theoretical value being 238.4.

The *sodium* salt forms stellate crystals, and is readily soluble in water, fairly so in alcohol. In benzene, ethyl acetate, or acetone it is insoluble.

The *barium* salt was precipitated as a granular powder on adding a solution of barium chloride to a neutral solution of the ammonium

salt. It is sparingly soluble in water, and crystallises well from aqueous alcohol:

0.3594 gave 0.1445 BaSO_4 . $\text{Ba} = 23.67$.

$\text{C}_{19}\text{H}_{24}\text{O}_6\text{S}_2\text{SiBa}$ requires $\text{Ba} = 23.76$ per cent.

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XVII.—*The Influence of Various Substituents on the Optical Activity of Tartramide. Part III. Halogen-substituted Anilides.*

By PERCY FARADAY FRANKLAND and DOUGLAS FRANK TWISS.

IN a previous communication (Trans., 1906, 89, 1852) we have given a list of the molecular rotations of the known tartramide derivatives, including the anilide and toluidides. In extension of this work we are now recording the results obtained with the chloroanilides and bromoanilides of tartaric acid, since it is of interest to study further the effect of substituents in the benzene ring of the anilide radicle. Previous investigations on asymmetric substances containing the benzene ring substituted in the different possible positions (for a list of papers see A. W. Stewart's *Stereochemistry*, p. 95; Betti, *Gazzetta*, 1907, 37, i, 62; and Pickard and Littlebury, Trans., 1907, 91, 300) have elicited the general result that the rotation of the isomerides stands in the order para \rightarrow meta \rightarrow ortho, exceptions being comparatively rare (compare Goldschmidt and Freund, *Zeitsch. physikal. Chem.*, 1894, 14, 394; also Frankland and Barrow, Trans., 1909, 95, 2031). The bromoanilides and chloroanilides described in this paper form no exception to the general rule, as is shown by the table given later.

In a previous communication on the ethyl and methyl esters of the *o*-, *m*-, and *p*-toluoyltartaric acids (Frankland and Wharton, Trans., 1896, 69, 1309 and 1583), it was also pointed out that the relative rotations of the ortho-substituted and of the unsubstituted aromatic compounds respectively appear to depend on both the centre of gravity of the chain attached to the asymmetric atom, and also on the increase in mass of the chain. If the loss in leverage is not compensated sufficiently by the increase in mass, the rotation of the substituted

molecule will be less than that of the unsubstituted; this was the case with the substitution of methyl in the ortho-position in benzoyl-tartaric esters.

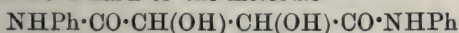
In the case of the anilides of tartaric acid, the substitution of methyl, bromine, or chlorine in the ortho-position lowers the molecular rotation; in the meta-position, the substitution of methyl causes a slight diminution, but the heavier chlorine or bromine an increase in the molecular rotation. This result is in all probability due mainly to the effect of the superior mass of the bromine and chlorine atoms, but may also be assisted to some extent by the negative character of these atoms, as explained later.

The following table gives the values for the molecular rotations (in pyridine solution) of the chloroanilides and bromoanilides, together with those already published for the toluidides and the anilide, the latter being included for the sake of comparison.

$[M]_D^{20^\circ}$ dianilide.	$[M]_D^{20^\circ}$ ditoluidide.	$[M]_D^{20^\circ}$ dibromoanilide.	$[M]_D^{20^\circ}$ dichloroanilide.
+739°	ortho +667° meta +730 para +793	+652° +867 +886	+709° +824 +838

A remarkable fact shown by these numbers is that, whilst the replacement of the ortho-hydrogen atom by methyl causes a lowering in the molecular rotation, replacement by the heavier substituent chlorine causes a much smaller decrease, and even the bromine atom hardly lowers the rotation of tartranilide more than the methyl group.

Again, it is noteworthy that in the series toluidide \rightarrow bromoanilide \rightarrow chloroanilide, the difference between the values of the meta- and para-isomerides becomes less. This effect, together with the one previously mentioned, is possibly due to the increase in the negative character of the substituent; we would suggest that the negative substituent in the meta-position of the benzene ring is attracted (probably by one of the hydrogen atoms in the tartaric acid nucleus) in such a direction that the resulting distortion increases the asymmetry, whilst with the negative atom in the para-position the differently directed attraction causes such distortion that the asymmetry is decreased. Thus the more negative the substituent, the more closely will the rotations of the meta- and para-isomerides approximate to one another. That this explanation is at least a reasonable one is seen by constructing a graphic formula of the most compact configuration of the molecule, with the bonds drawn to the correct angles and to lengths in accord with Traube's atomic volumes. In such a formula the chain $C \cdot CH \cdot CO \cdot NHPh$ of the molecule



will be found to form an almost closed ring, the hydrogen attached

to the one asymmetric carbon atom falling near the benzene ring and actually between the meta- and para-positions of the chain attached to the other asymmetric atom. Any attraction between this hydrogen atom and a halogen atom in the para-position of the benzene ring will cause an increased compactness of the molecule, and so lessen the asymmetry. On the other hand, an attraction between this hydrogen and a negative atom in the meta-position will lead to a distortion outwards, from the tartaric nucleus, and so cause an outward displacement of the $\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{X}$ chain, with a corresponding increase in asymmetry.

A halogen atom in the ortho-position would probably be so far removed from the hydrogen of the other asymmetric atom that the attraction would be much less; nevertheless, the experimental results seem to indicate that even this has an appreciable effect in increasing the asymmetry.

In connexion with this hypothesis it is of interest to compare the rotation of the *m*-iodotartranilide* with that of the other meta-substituted tartranilides.

	Dianilide.	Di-toluidide.	Dichloro-anilide.	Dibromo-anilide.	Di-iodo-anilide.
$[\text{M}]_D^{20}$ (in pyridine solution)	739°	730°	824°	867°	888°
Increase in rotation	-9°	94°	43°	21°	
Increase in mass (for one chain)	14	20.5	44.5	47	

The increase in $[\text{M}]_D$ is greatest for one of the smallest changes in mass, and it is remarkable that it is between the neutral methyl and the negative chlorine. For the increase in optical activity between the chloro- and bromo-anilide, the mass-increase is the cause, the inferior negativity of the bromine atom reducing the $[\text{M}]_D$ and so giving rise to a smaller increment in activity. Again, the diminished negativity of the iodine atom would be the reason for the greatest increase in mass (47) being attended, nevertheless, by the smallest increment in activity.

In the preparation of the compounds described in this paper, great care was taken to ensure a pure product. Each substance, where possible, was prepared in two ways (from the free acid and from the methyl ester), and the product was in each case recrystallised until of constant specific rotation. The majority of the rotations were measured in approximately 5 per cent. solution in dry pyridine at 20°. Concentration was found to have little influence on the optical activity. The substances were all crystalline solids of high melting point (185—276°).

* Prepared by Mr. Norton in this laboratory; this, with other iodoanilides, will form the subject of a future communication.

EXPERIMENTAL.

Tartarodi-p-bromoanilide.

This was prepared by heating together powdered tartaric acid and *p*-bromoaniline (Kahlbaum) in theoretical proportions at 150—160° for fifteen hours. After extracting with boiling dilute hydrochloric acid and with water, the residue was repeatedly crystallised from a mixture of alcohol and pyridine (7 : 3 by volume).

The following figures show the rotation observed in pyridine solution :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.902	1.0004	1.998	+18.95°	+193.4°	+886°

The substance was also prepared by heating together theoretical proportions of methyl tartrate and *p*-bromoaniline to 130—140° for ten hours. After similar purification to that described above, the product gave the following rotation in pyridine solution :

4.908	1.0003	1.998	+18.95°	+193.2°	+885°
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The rotation in methyl alcohol is not suited for exact measurement on account of the low solubility of the substance ; the result, however, indicates a distinctly lower rotatory power than that in pyridine solution :

0.1359	0.792	3.899	+0.76°	+181.1°	+829°
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The specimens of bromoanilide prepared by the above methods had the same melting point, namely, 264° with decomposition ; the substance forms slender crystals (elongated flat plates), which become matted together so as to give rise to a tough white solid resembling paper. It is insoluble in water, sparingly soluble in most of the ordinary solvents, but readily so in pyridine :

0.2429 gave 12.68 c.c. N₂ (moist) at 11.8° and 754 mm. N = 6.12.

C₁₆H₁₄O₄N₂Br₂ requires N = 6.12 per cent.

Tartarodi-m-bromoanilide.

As with the para-compound, this was prepared by the two independent methods. The tartaric acid and *m*-bromoaniline (Kahlbaum) were heated to 150—160° for ten hours, and the methyl tartrate and base to 130—140° for the same period. The product is more soluble in alcohol than the para-compound, and, after extraction with dilute hydrochloric acid, was purified by recrystallisation from this solvent.

The following numbers give the rotation observed in pyridine solution :

(a) Preparation from tartaric acid and *m*-bromoaniline :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4·817	0·9995	1·998	+18·22°	+189·4°	+867°

(b) Preparation from methyl tartrate and *m*-bromoaniline :

4·835	0·9994	1·998	+18·28°	+189·3°	+867°
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The rotation of the specimen prepared from tartaric acid was also measured in methyl-alcoholic solution :

0·9862	0·7981	3·899	+4·74°	+154·5°	+707°
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The *m*-bromoanilide crystallises in small, hard, flat plates, which melt at 220° with slight decomposition :

0·2716 gave 14·3 c.c. N₂ (moist) at 13° and 753 mm. N = 6·14.

C₁₆H₁₄O₄N₂Br₂ requires N = 6·12 per cent.

Tartarodi-o-bromoanilide.

This substance was prepared only from tartaric acid and *o*-bromoaniline, the mixture of methyl tartrate and *o*-bromoaniline undergoing extensive decomposition on heating. Approximately theoretical proportions of tartaric acid and *o*-bromoaniline (from reduction of *o*-bromonitrobenzene: Fittig and Mager, *Ber.*, 1874, 7, 1179) were heated to 150—160° for twenty hours. The resultant mass was purified by treatment similar to that in the previous cases, and, finally, repeatedly recrystallised from a mixture of alcohol and water (3 : 2 by volume) with simultaneous decolorisation by animal charcoal.

The optical activity was measured in pyridine and in methyl alcohol :

(a) In pyridine :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
6·604	1·0076	0·999	+9·46°	+142·3°	+652°
4·572	0·9989	0·999	6·53	143·1	656

(b) In methyl alcohol :

3·363	0·8076	0·999	+3·21°	+118·3°	+542°
0·9402	0·7964	2·993	2·71	120·9	554

The *o*-bromoanilide consists of colourless, thin, rectangular needles, which melt at 193° without decomposition; it is very soluble in pyridine and in hot alcohol, and sparingly so in hot water :

0·2410 gave 12·9 c.c. N₂ (moist) at 17·5° and 745 mm. N = 6·04.

C₁₆H₁₄O₄N₂Br₂ requires N = 6·12 per cent.

Tartarodi-p-chloroanilide.

The method of preparation was similar to that of the corresponding bromoanilide; the substance was purified by recrystallisation from a mixture of 1 volume of pyridine to 3 of alcohol.

Preparation from tartaric acid, in pyridine solution :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.605	0.9939	1.998	+20.77°	+227.1°	+838°

Preparation from methyl tartrate, in pyridine solution :

5.015	0.9957	0.999	+11.34°	+227.3°	+839°
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The rotation in methyl-alcoholic solution was much lower than that observed in pyridine, although the low solubility increases the probability of error in the specific rotation :

0.1749	0.7943	3.899	+1.06°	+196°	+722°
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The *p*-chloroanilide forms needle-shaped crystals, melting and decomposing at 276° :

0.2035 gave 13.6 c.c. N_2 (moist) at 12.6° and 748 mm. $N = 7.75$.

$C_{10}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

Tartarodi-m-chloroanilide.

The reaction, both in the case of the preparation from the acid and *m*-chloroaniline (Kahlbaum), as well as in that from the ester and base, appeared to proceed less rapidly than in the production of *m*-bromoanilide, and involved heating for sixteen hours. After the usual preliminary treatment, the product was recrystallised from a mixture of 1 volume of water with 3 of alcohol.

The specimen from tartaric acid and *m*-chloroaniline gave the following rotation in pyridine solution :

<i>p.</i>	<i>d</i> 20°/4°.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.966	0.9953	0.999	+11.03°	+223.4°	+824°
1.746	0.9829	2.993	11.42	222.3	820

whilst that from methyl tartrate and the base gave the following figures :

4.865	0.9949	0.999	+10.80°	+223.4°	+824°
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The rotation in solution in methyl alcohol was as follows :

1.504	0.7971	2.993	+6.54°	+182.3°	+673°
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Tartarodi-m-chloroanilide crystallises in thin, fibrous needles, which melt and decompose slightly at 212° :

0.2035 gave 13.7 c.c. N_2 (moist) at 13° and 735 mm. $N = 7.66$.

$C_{16}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

Tartarodi-o-chloroanilide.

As in the case of the corresponding *o*-bromoanilide, the preparation of this substance was attended with more difficulty than that of the meta-compound; the mixtures had to be heated for twenty hours, and the yields were inferior to those obtained in the case of any of the other anilides. The yield from the ester was particularly poor, the crude product being a black, pasty mass. For the recrystallisation a mixture of one part of water to two of alcohol was employed.

The following are the rotations obtained in pyridine solution :

(a) Specimen prepared from tartaric acid :

<i>p.</i>	<i>d</i> $20^\circ/4^\circ$.	<i>l</i> (dms.).	$\alpha_D^{20^\circ}$.	$[\alpha]_D^{20^\circ}$.	$[M]_D^{20^\circ}$.
4.881	0.9944	0.999	+9.32°	+192.2°	+709°
1.392	0.9816	2.993	7.89	192.9	712

(b) Specimen from methyl tartrate :

5.060	0.9940	0.999	+9.65°	+192.1°	+709°
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The optical activity was measured also in methyl alcohol :

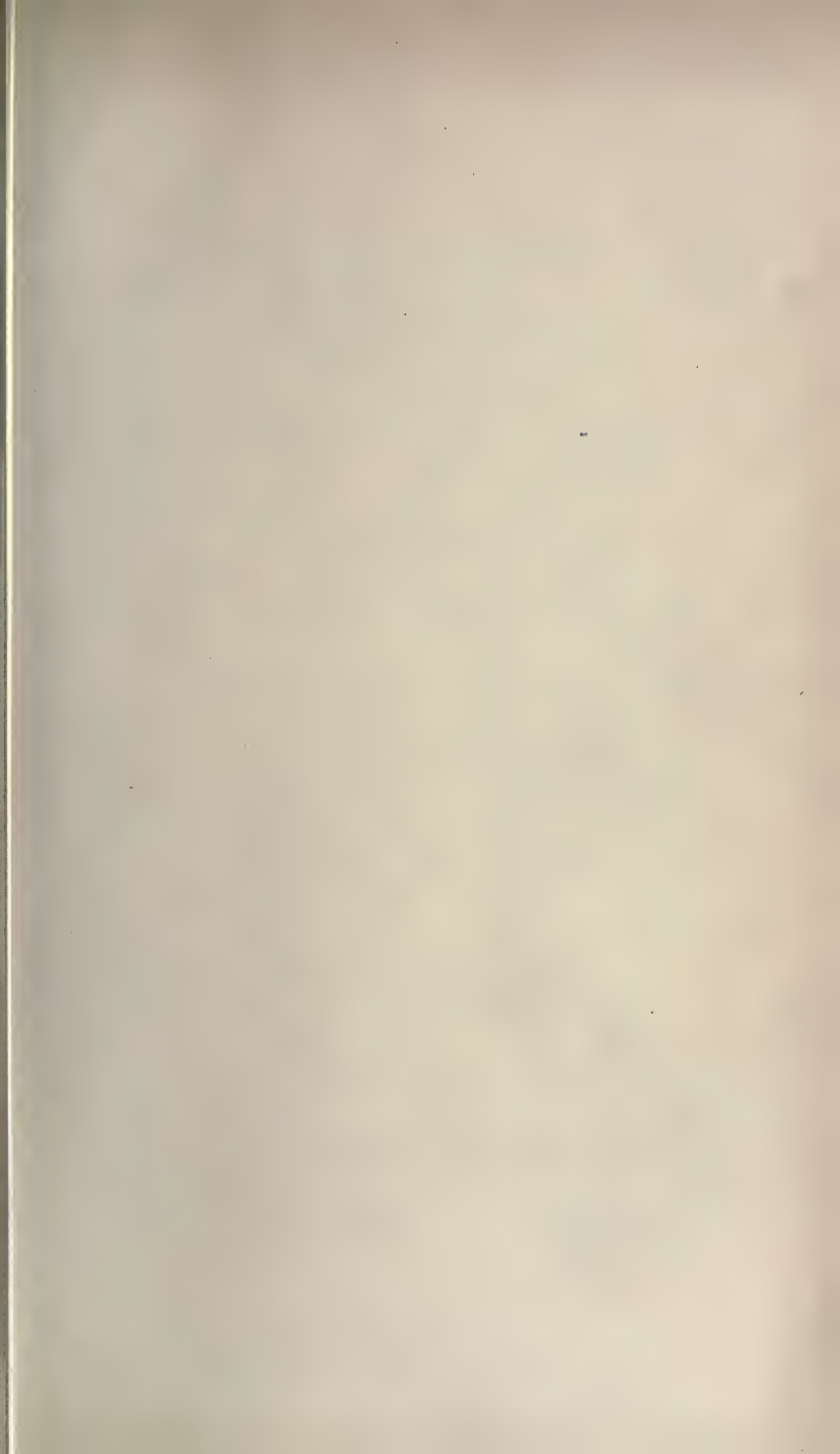
1.524	0.7980	2.993	+5.98°	+164.3°	+606°
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The *o*-chloroanilide crystallised in long, narrow plates, melting at 185° . It is sparingly soluble in hot water, but very soluble in pyridine and in hot alcohol :

0.2067 gave 13.75 c.c. N_2 (moist) at 14° and 748 mm. $N = 7.67$.

$C_{16}H_{14}O_4N_2Cl_2$ requires $N = 7.59$ per cent.

UNIVERSITY,
BIRMINGHAM.





THOMSEN MEMORIAL LECTURE.

DELIVERED ON FEBRUARY 17TH, 1910.

By SIR EDWARD THORPE, C.B., LL.D., F.R.S., Past-President of the Chemical Society.

AMONG the Danes whose names are inscribed as men of science on the eternal bead-roll of fame, that of Julius Thomsen stands pre-eminent—linked indeed with that of Oersted. It is significant of the position which Thomsen acquired in physical science, and of the respect which that position secured for him in the eyes of his countrymen, that his statue should have been erected during his lifetime and placed in the vicinity of that of Oersted in the courtyard of the Polytechnic High School of Copenhagen. Thomsen, in fact, played many parts in the intellectual, industrial, and social development of Denmark. To Europe in general he was mainly known as a distinguished man of science. By his fellow-citizens he was further recognised as an educationist of high ideals, actuated by a strong common sense and a stern devotion to duty; as an able and sagacious administrator; as a successful technologist and the creator of an important and lucrative industry based upon his own discoveries; and as a man of forceful character, who brought his authority, skill, and knowledge of men and affairs to the service of the communal life of Copenhagen.

Thomsen was a municipal councillor of that city for more than a third of a century. He occupied a commanding position on the Council, and was invariably listened to with respect. The gas, water, and sewage works of Copenhagen are among the monuments to his civic activity. From 1882 up to the time of his death he was a member of the Harbour Board of the port. In these respects Thomsen sought to realise Priestley's ideal of the perfect man—that he should be a good citizen first and a man of science afterwards.

Hans Peter Jürgen Julius Thomsen was born in Copenhagen on February 16th, 1826. He was educated at the church school of St. Peter in that city, and subsequently at von Westens Institute. In 1843 he commenced his studies at the Polytechnic, and in 1846 graduated there in Applied Science, and became an assistant to Professor E. A. Scharling. Of his earliest years comparatively little is known. Thomsen, always a reserved and taciturn man, talked little about himself even to his intimate friends—and least of all about the days of his youth. It was known to a few that these days had not been smooth. Those who were best informed

were conscious that to these early struggles much of that dour and resolute nature which formed a distinguishing trait in his character was due. Thomsen, indeed, began life as a fighter, and a fighter he remained to the end of his four-score years.

In 1847, he became assistant to Forchhammer, passing rich, like Goldsmith's pedagogue, on £40 a year. Georg Forchhammer, whose earliest work dates back to the period when Berzelius was in his prime, was an active and industrious investigator of the old school, mainly in inorganic chemistry, and more particularly on problems of chemical geology and physiography. He was a frequent visitor to this country, and was well known to early members of the British Association. Although doubtless influenced, in common with all teachers in Northern Europe, by the example and methods of Berzelius, such influence as he himself was able to exert died with him. Forchhammer attracted few pupils, and created no school, and Thomsen probably derived no inspiration or acquired any stimulus from this association. For a time Thomsen supplemented his scanty income by teaching agricultural chemistry at the Polytechnic. In 1853 he obtained a travelling scholarship, and spent a year in visiting German and French laboratories. He probably owed this scholarship in great measure to his first contribution to the literature of chemistry, namely, his memoir, "Bidrag til en Thermochemisk System" (contributions to a thermochemical system), communicated to the Royal Society of Sciences of Copenhagen in 1852, and for which he received the silver medal of the Society and a sum of ten guineas to enable him to procure a more accurate apparatus. In this memoir he sought to develop the chemical side of the mechanical theory of heat, doubtless under the influence of Ludwig Augustus Colding, an engineer in the service of the Municipality of Copenhagen, and a pioneer, like Mayer, in the development of that theory. Indeed, the Danes now claim for Colding, who had made experiments on the relation between work and heat as far back as 1842, but whose labours were practically ignored by his contemporaries, the position which the Germans assign to Mayer (see Mach's "Development of the Theory of Heat"). In 1861 Thomsen further developed his ideas in a memoir on the "General Nature of Chemical Processes, and on a Theory of Affinity Based Thereon," published in the Transactions of the Danish Academy of Sciences. In this paper he laid the foundations of the chief scientific work of his life.

In 1853 Thomsen patented a method of obtaining soda from cryolite, so-called "Greenland," or ice-spar, a naturally occurring fluoride of sodium and aluminium, $\text{Al}_2\text{F}_6 \cdot 6\text{NaF}$, found largely, indeed, almost exclusively, in Greenland, and particularly at

Ivigtut. It derives its mineralogical name from its ice-like appearance and ready fusibility even in the flame of a candle. It seems to have been first brought to Europe in 1794, and to have been described by Schumacher in the following year. Klaproth first showed that it contained soda, and its composition was further established by Vauquelin, Berzelius, and Deville.

Thomsen's process consists in heating a finely divided mixture of cryolite and chalk in a reverberatory furnace, whereby carbon dioxide is expelled and calcium fluoride and sodium aluminate are formed. The roasted mass is lixiviated with water, so as to dissolve out the sodium aluminate, which is then treated with carbon dioxide. Alumina is precipitated, and sodium carbonate remains in solution. The alumina is either sold as such, or converted into sulphate (so-called "concentrated alum" or "alum-cake"), and the sodium carbonate is separated by crystallisation. Both products are obtained in a remarkably pure condition, and the cryolite-soda yields excellent "caustic."

Thomsen's process, although simple enough in principle, requires considerable skill and pains in its practical execution, and most of the manufacturing details were worked out by him, or under his direction. Success largely depends upon the maintenance of a proper temperature; the decomposition begins below a red-heat, but requires to be finished at that temperature, and care must be taken to avoid fusion or even sintering of the mass. In 1854 Thomsen obtained the exclusive right of mining for cryolite and of working up the mineral in Denmark for soda and alumina. Actual manufacturing operations were begun on a small scale in 1857, and in the following year Thomsen planned the present large factory at Oeresund, near Copenhagen, which was opened on his thirty-fourth birthday. The importance of this industry to Denmark may be seen from the circumstance that during the fifty years of its existence the firm have paid the Danish Government nearly £300,000 for the concession. Other factories were started in Germany, Bohemia, and Poland, but met with little success. The Pennsylvania Salt-manufacturing Company at Natrona, near Pittsburg, eventually obtained the right to work up two-thirds of all the cryolite mined in Greenland. From the start Thomsen took a large share in the management of the Oeresund works, and by his energy, foresight, and skill placed the undertaking on a sound commercial basis.

Although Thomsen died a rich man, mainly as the result of the industry he created, in the outset of his career as a teacher and a technologist his means were very straitened. He came of poor parents, of no social position or influence, and they were unable to

further his inclinations towards an academical career. In 1854 he applied unsuccessfully for a position as teacher of chemistry at the Military High School in Copenhagen. During three years—from 1856 to 1859—while still engaged in developing his cryolite process, he acted as an adjuster of weights and measures to the Municipality of Copenhagen. It was a poorly paid position, but it kept the wolf from the door. At about this period he betook himself to literature, and published a popular book on general subjects connected with physics and chemistry—somewhat in the style of Helmholtz's well-known work—entitled "Travels in Scientific Regions," which had a considerable measure of success. He was, however, not altogether unknown even at this time as an author, since in 1853 he had collaborated with his friend Colding in producing a memoir on the causes of the spread of cholera and on the methods of prevention, which attracted much attention at the time of its appearance.

In 1859, whilst engaged in the Oeresund factory, he again applied to the authorities for a position as teacher at the Military High School, and succeeded in obtaining an appointment to a lectureship in physics, which he held until 1866. During his tenure of this office he devised his polarisation battery, which received many awards at International Exhibitions and was used for a time in the Danish telegraph service.

In 1859-60 he was "vicarius" for Scharling at the University, and in 1865 became a teacher, and in the following year Professor of Chemistry and Director of the Chemical Laboratory, a position which he retained—active to the last—until 1901, when he retired in his seventy-fifth year of age.

Before his connexion with the University, he founded and edited, from 1862 to 1878, in association with his brother, August Thomsen, the *Journal of Chemistry and Physics*, one of the principal organs of scientific literature in Denmark.

In 1863 he was elected a member of the Commission of Weights and Measures, and was instrumental in bringing about the adoption of the metric system and the assimilation of the Danish system to that of the Scandinavian Kingdom.

In 1883 Thomsen became Chancellor of the Polytechnic High School of Copenhagen—a position which he held for about nine years. During this period he entirely changed the character and spirit of the school, and stamped it with the impress of his earnestness and industry. Under his direction, new buildings were erected and arranged in accordance with the best Continental and American models. Thomsen's administration was in marked contrast to that of his somewhat easy-going predecessor, but it is doubtful if it

brought him popularity in the school. The students respected and even feared him, but his cold and unsympathetic nature evoked no warmer feeling. It was said of him by one who knew him intimately that he never learned to draw the young to him, to create in them an interest for his work, to form a school. Thomsen was a homely man, but not even in his home, says the same authority, was it possible for him to change his active, earnest, strenuous disposition—what his friends called his fighting character. But if he was always the serious master of the house, he was also its obedient servant. In reality he was a man of deep feeling, and was not without power to give that feeling expression in words, sometimes in verse, and occasionally even in music.

It was while occupying the position of Director of the Chemical Laboratory of the University that Thomsen executed the thermochemical investigations which constitute the experimental development of the ideas he had formulated in his memoir of 1861. The results of these inquiries were first made known in a series of papers published from 1869 to 1873 in the Transactions of the Royal Danish Society of Sciences, and from 1873 onwards by the *Journal für Praktische Chemie*. The papers were republished in collected form in four volumes (1882-1886) by a Leipzig house under the title of *Thermochemische Untersuchungen*. A summary of this experimental labour, which extended over a third of a century, was subsequently prepared by Thomsen, and published in 1905 in Danish under the title of *Thermokemiske Resultater*.

In this work he reviewed the whole of the numerical and theoretical results, to the exclusion of the greater portion of the experimental details. A translation of this volume by Miss Katharine A. Burke, entitled "Thermochemistry," renders it readily accessible to English readers. Miss Burke has supplemented the original work by a short account, taken from the *Thermochemische Untersuchungen*, of the experimental methods employed, thereby rendering the whole more intelligible to the student. Moreover, in the English edition a partial attempt has been made to translate Thomsen's deductions into the language of modern theory based on the conception of ionisation, which, of course, was not known to science at the time the *Thermochemische Untersuchungen* was published.

It is impossible within the limits of such a notice as this to deal in detail with the immense mass of experimental material which this work embodies, and I shall not attempt, therefore, to do more than to offer a generalised statement, based mainly upon the admirable account of Thomsen's work given by Professor Brönsted to the Chemical Society of Copenhagen on the occasion of the

meeting held on March 2nd, 1909, to commemorate Thomsen's services to science.

The conception of affinity as a cause and determining condition of chemical change is traceable in some of the earliest efforts to co-ordinate and explain chemical phenomena. It certainly existed long prior to the time of Boyle, and was at the basis of every philosophical system after his period. We need only mention the names of Bergman, Wenzel, and Berthollet to indicate this fact. But to Thomsen belongs the credit of being the first to make the attempt to measure the relative value or strength of affinity quantitatively, and to express it numerically in definite terms which admitted of exact comparison. Thomsen's theory of affinity, as enunciated by him in his 1851 paper, was based upon his conviction that affinity could be measured quantitatively by estimating the amount of heat evolved in the chemical process. We are not immediately concerned to show whether the theory is right or wrong, or in what respect it fails. The point is that the enunciation of this principle upwards of half a century ago constituted an important step forward, inasmuch as it sought to estimate affinity in relation to a quantity which can be fixed by experiment, and is capable of expression by numbers.

In this and in the subsequent paper of which mention has been made already, he thus defines his conception of thermochemistry, and discusses, for the first time, its laws.

"The force which unites the component parts of a chemical compound is called affinity. If a compound is split up, whether by the influence of electricity, heat, or light, or by the addition of another substance, this affinity must be overcome. A certain force is required the amount of which depends on the strength of the affinity.

"If we imagine, on the one side, a compound split up into its component parts, and on the other side these parts again united to form the original compound, then we have two opposite processes the beginning and end of which are alike. It is therefore evident that the amount of the force required to split up a certain compound must be the same as that which is evolved if the compound in question is again formed from its component parts.

"The amount of force evolved by the formation of a compound can be measured in absolute terms; it is equal to the amount of heat evolved by the formation of the compound.

"Every simple or complex action of a purely chemical nature is accompanied by evolution of heat.

"By considering the amount of heat evolved by the formation of a chemical compound as a measure of the affinity, as a measure

of the work required again to resolve the compound into its component parts, it must be possible to deduce general laws for the chemical processes, and to exchange the old theory of affinity, resting on an uncertain foundation, for a new one, resting on the sure foundation of numerical values."

As has been proved by later theoretical and experimental investigations, the theory of thermochemical affinity is not absolutely correct at ordinary temperatures. But, on the other hand, it has been shown that a comparatively large number of processes are approximately in unison with it. Not only do they agree qualitatively, that is to say, that heat is evolved during the process, but also in the fact that the results which newer and more exact methods for estimating affinity have produced, agree numerically with what would be required by the thermochemical theory. We meet here with a fundamental phenomenon which Thomsen deserves great credit for having first pointed out, but the explanation of which could not be given at the time he indicated it. It can be demonstrated theoretically that the lower we reduce the temperature and the nearer we get to the absolute zero, the more nearly is the condition for the theory fulfilled, so that at the absolute zero the theory would be found to be an exact law of nature. If it were possible to work at such low temperatures it would be found that the evolution of heat, or the evolution of energy by the chemical process, would be an exact measure of the affinity of the process, and that under this condition the theory of Thomsen would be the accurate expression of a natural law.

But under ordinary conditions this is not so, for in reality an ever-increasing number of endothermic processes are found to occur, that is, processes which proceed with the absorption of heat. Thomsen tried at first to explain these phenomena in such a way as to keep them within his system, and he drew a distinction between a purely chemical process running conformably to his theory and a physico-chemical process which did not fall within the law. But he was gradually convinced that his theory could not be maintained in its entirety. It is to his credit that he did not seek to uphold an untenable principle, or try to defend it as did Berthelot, who almost to his dying day maintained the validity of the principle in spite of all facts.

These ideas have, in the words of Ostwald, been the scientific confession of faith of chemists throughout half a century. They have had the greatest influence on scientific thought in every branch of chemistry. It is on the basis of them that we have arrived at a theory of affinity which at the present moment is being developed into one of the most perfect chemical theories.

Lastly, it is due to these ideas that the experimental material has been produced which during all time will place the name of Julius Thomsen in the first rank of men of science.

To go through this material in detail is, as I have said, impossible here. It may be stated generally that practically every simple inorganic process has been investigated calorimetrically by Thomsen, or can be calculated by means of the calorimetric data furnished by him. In the case of organic substances, data have been given for estimating the heat of combustion of a large number of compounds. All these estimations were made by Thomsen personally, according to a pre-arranged plan, and in systematic succession during a period of more than thirty years. They comprise more than 3500 calorimetric estimations. It has been truly said that this work is unique in the chemical history of any country.

Among the results of Thomsen's thermochemical inquiries which have special value for physical chemistry is his investigation of the phenomena of neutralisation, in which he shows that the basicity of acids can be estimated thermochemically, and that it can in this way be proved whether or not a point of neutrality exists. His observation that the heat of neutralisation is the same for a long series of inorganic acids, such as hydrochloric acid, hydrobromic acid, hydriodic acid, chloric acid, nitric acid, etc., supports the theory of electrical dissociation, inasmuch as this requires that the heat of neutralisation of the strong acids must in all cases be independent of the nature of the acid, because the process of neutralisation for all of them is the combination of the ion of hydrogen in the acid with the ion of hydroxyl of the base to form water. These investigations also led to the important thermochemical result that the heat of neutralisation of acids (or the heat of their dissociation) cannot be considered as a measure of the strength of the acids.

Another important result is the proof by experiment of the connexion which exists between the changes of the heat-effect with the temperature and the specific heat of the reacting substances. The first law of thermodynamics requires the relation indicated by Kirchhoff: $\frac{dU}{dT} = C_1 - C_2$, where U is the heat-effect, T the temperature, and C_1 and C_2 are the heat capacities of the two systems before and after the reaction, and Thomsen showed by investigation of the heat of neutralisation, the heat of solution, and the heat of dilution, that this relation was satisfied. For the purpose of his inquiry, the specific heats of a large number of solutions of salts were estimated by an ingenious method, and with an exactness hitherto unattained.

Of no less importance are Thomsen's thermochemical investigations on the influence of mass. In the year 1867 Guldberg and Waage published their theory of the chemical effect of mass. But they had only verified the theory to a small extent and in particularly simple cases. They had not investigated the complete homogeneous equilibrium, because at that time no method existed for experimental investigation of such homogeneous equilibrium. Thomsen showed that the estimation could be made thermochemically. By allowing, for instance, an acid to act on a salt of another acid in an aqueous solution, the latter acid will be partly replaced by the first, which will form a salt. By mixing, for instance, a solution of sodium sulphate and nitric acid, there is formed sodium nitrate and sulphuric acid, but the process will not proceed to completion. If we have estimated the heat of neutralisation of the two acids with sodium hydroxide, the difference between these two heat-phenomena will give the amount of heat corresponding to the total decomposition of the sodium sulphate, and the heat found experimentally by mixing the two solutions will therefore show to what degree the transformation has taken place. It would be possible to estimate thermochemically the amount of the four substances in solution, and thereby, by varying the concentration or the proportion between the initial quantities of substances, to calculate whether the Guldberg-Waage theory on the effect of mass was confirmed in this case.

Thomsen applied this method to a large number of different acids and bases, and was enabled thereby to prove the agreement with the law of the influence of mass in all the cases which he examined. He found particularly that the proportion of the one acid which remained combined with the base was constant with mixtures of constant proportion. On this basis he propounded the term *avidity*, which he defined as the tendency of the acid to unite with the base, and he showed that the avidity was independent of the concentration, and only to a small extent varied with the temperature. The term avidity has since acquired great importance, particularly since other and more exact methods for its estimation have been found. Concurrently with this, its meaning has been made clear by the theory of electrolytic dissociation.

On the basis of these estimations, Thomsen drew up the first table, based on experiments, of the relative strength of the acids, and the numbers in this table have been found to agree with the results obtained by examining the electrical conductivity of the acids.

It is worth noting that Thomsen not only produced the experimental proof of the correctness of the Guldberg-Waage theory of

the effect of mass soon after the appearance of this theory, but also that he was the first to acknowledge and adopt it. It is remarkable that this work of Thomsen received so little attention, although it appeared in a widely circulated German journal, and it was not until ten years later that the law of the effect of mass was generally recognised, as the result of the work of Ostwald and van't Hoff.

Although Thomsen's title to scientific fame rests mainly upon his thermochemical work, his interests extended beyond this particular department of physical chemistry. He worked on chloral hydrate, selenic acid, on ammoniacal platinum compounds, and on glucinum platinum chloride, on iodic acid and periodic acid, on hydrogen peroxide, hypophosphorous acid, and hydrogenium. He early recognised the importance of Mendeléeff's great generalisation, and contributed to the abundant literature it produced. His paper of 1895, "On the Probability of the Existence of a Group of Inactive Elements," may be said to have foreshadowed the discovery of the congeners of argon. He pointed out that in periodic functions the change from negative to positive value, or the reverse, can only take place by a passage through zero or through infinity; in the first case, the change is gradual, and in the second case it is sudden. The first case corresponds with the gradual change in electrical character with rising atomic weight in the separate series of the periodic system, and the second case corresponds with a passage from one series to the next. It therefore appears that the passage from one series to the next in the periodic system should take place through an element which is electrically indifferent. The valency of such an element would be zero, and therefore in this respect also it would represent a transitional stage in the passage from the univalent electronegative elements of the seventh to the univalent electropositive elements of the first group. This indicates the possible existence of a group of inactive elements with the atomic weights 4, 20, 36, 84, 132, the first five numbers corresponding fairly closely with the atomic weights respectively of helium, neon, argon, krypton, and xenon (*Zeitsch. anorg. Chem.*, 1895, **9**, 283; *Journ. Chem. Soc.*, 1896, **70**, II, 16). He subsequently made known the existence of helium in the red fluorite from Ivigtut.

As evidence of Thomsen's manipulative ability and his power of accurate work may be mentioned his determination of the atomic weights of oxygen and hydrogen, and incidentally of aluminium. For the atomic weight of hydrogen he obtained the value 1.00825 when O=16, which is practically identical with that of Morley and Noyes. He further made most accurate estimations of the relative

densities of these gases, and of the volumetric ratios in which they enter into the composition of water. His value for the atomic weight of aluminium is nearly identical with that adopted in the last Report of the International Committee on Atomic Weights.

Thomsen maintained his interest in thermochemical problems up to the end, and was a keen and clear-sighted critic of the work which appeared from time to time during the later years of his life. This interest occasionally gave rise to controversy, and some of his latest papers were wholly polemical.

Thomsen was a pronounced atomist, and to him a chemical process was a change in the internal structure of a molecule, and the chief aim of chemistry was to investigate the laws which control the union of atoms and molecules during the chemical process. He considered that chemistry should be treated mathematically as a branch of rational mechanics. But no one insisted more strongly than he how little we really know of these questions. In summarising his theoretical ideas in the *Thermokemische Resultater*, he says, "An almost impenetrable darkness hides from us the inner structure of molecules and the true nature of atoms. We know only the relative number of atoms within the molecule, their mass, and the existence of certain groups of atoms or radicles in the molecule, but with regard to the forces acting within the molecules and causing their formation or destruction our knowledge is still exceedingly limited." He fully realised that his own work was only the foundation on which the future elucidation of these questions must rest. "He worked," says Brönsted, "in the conviction that what we somewhat vaguely call the affinity of the atoms—their interaction, their attraction, and varying effect, etc.—follows the general laws of mechanics, and that, as he worded it, the principle that 'might is right,' holds good in chemistry as in mechanics. On this foundation he hoped to be able to evolve the laws for the statics and dynamics of chemical phenomena, even although the true nature of the action is unknown."

Thomsen's merits as an investigator received formal recognition from nearly every country in the civilised world. As far back as 1860 he was elected one of the thirty-five members of the Danish Royal Society of Sciences of Copenhagen, and from 1888 until his death he was its President. In 1876 he became an Honorary Foreign Member of the Chemical Society of London. On the occasion of the fourth centenary of the foundation of the University of Upsala (created in 1477), he received the degree of Doctor of Philosophy *honoris causa*. In 1879 he was made an honorary M.D. of the University of Copenhagen. Two years later he was made a

Foreign Member of the Physiographical Society of Lund, and in 1888 he was elected a member of the Society of Science and Literature of Gothenburg. In 1885 he became a member of the Royal Society of Sciences of Upsala, and in 1886 of the Stockholm Academy of Sciences.

In 1883 he and Berthelot were together awarded the Davy Medal of the Royal Society—a fitting and impartial recognition on the part of the Society of the manner in which the two investigators, whose work not infrequently brought them into active opposition, had jointly and severally contributed to lay the foundations of thermochemistry.

In the same year Thomsen was made a member of the Accademia dei Lincei of Rome, and in the following year he was elected into the American Academy of Arts and Sciences in Boston, and of the Royal Academy of Sciences of Turin. In 1887 he was made a member of the Royal Belgian Academy.

In 1886-87 and again in 1891-92 he was Rector of the University of Copenhagen. In 1888 he became Commander of the Dannebrog, and in 1896, and on his seventieth birthday, he was made Grand Commander of the same order. On the same occasion the Danish chemists caused a gold medal to be struck in his honour. In 1902 he became a Privy Counsellor (Geheime Konferenz raad). In the same year he was elected a Foreign Member of the Royal Society of London.

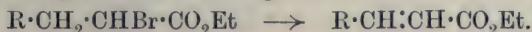
He died on February 13th, 1908, full of years as of honours, and was buried on the eighty-third anniversary of his birth and on the jubilee of the opening of the Oeresund factory. His wife, Elmine Hansen—the daughter of a farmer on Langeland—predeceased him in 1890.

I desire to express my acknowledgments to Director G. A. Hagemann, of Copenhagen, and to Professor Arrhenius, of Stockholm, for their assistance in obtaining information concerning Thomsen's personal history. I am also much indebted to our Fellow, Mr. Harald Faber, for his kindness in making for me a translation of Professor Brönsted's account of Thomsen's scientific work, on which my own résumé is mainly based.

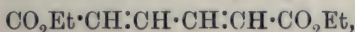
XVIII.—*Formation of Heterocyclic Compounds. Part II. Action of Bases on the $\alpha\alpha'$ -Dibromo-derivatives of Certain Dicarboxylic Acids.*

By HENRY RONDEL LE SUEUR and PAUL HAAS.

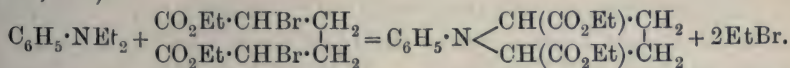
THE action of diethylaniline on aliphatic compounds containing bromine, and more especially on the esters of α -bromo-monocarboxylic acids (Crossley and Le Sueur, *Trans.*, 1899, **75**, 161; 1900, **77**, 83), is to remove the elements of hydrogen bromide with the formation of the corresponding unsaturated compound:



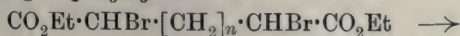
This action has been regarded as quite a general one, and holds good in the majority of instances. In the case of ethyl $\alpha\delta$ -dibromoadipate, $CO_2Et \cdot CHBr \cdot [CH_2]_2 \cdot CHBr \cdot CO_2Et$, a compound in which the two bromine atoms are separated from each other by four carbon atoms, the action of diethylaniline is quite different. Here it is true small quantities of the unsaturated ester, ethyl muconate,



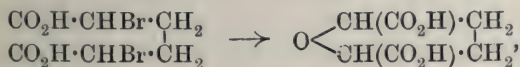
are formed, but by far the main product of the reaction is ethyl 1-phenylpyrrolidine-2:5-dicarboxylate (Le Sueur, *Trans.*, 1909, **95**, 276):



This reaction involves the fission of the two ethyl groups in diethylaniline, a change which is generally not easily effected, but that this actually takes place was proved by the isolation and identification of large quantities of ethyl bromide resulting from the above reaction. The action of aniline is quite similar to that of diethylaniline, as is shown by the action of aniline on methyl $\alpha\delta$ -dibromoadipate when the corresponding pyrrolidine ester is produced. The usual action of aniline on compounds of this type is to replace the bromine atom by the group $C_6H_5 \cdot NH$:

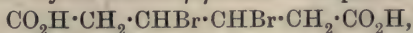


This great tendency for the formation of a five-membered ring is further illustrated by the action of alcoholic potassium hydroxide on $\alpha\delta$ -dibromoadipic acid, whereby *cis*-tetrahydrofuran-2:5-dicarboxylic acid is produced:



the usual action of alcoholic potassium hydroxide, namely, the removal of hydrogen bromide and formation of the corresponding unsaturated compound, only taking place to a small extent, as only small quantities of muconic acid were obtained.

In contrast to the above reaction, we may compare the action of alcoholic potassium hydroxide on $\beta\gamma$ -dibromoadipic acid,



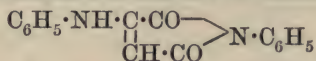
whereby Rupe (*Annalen*, 1890, 256, 1) obtained an 85 per cent. yield of muconic acid. In the bromo-acid employed by Rupe, the two bromine atoms are attached to adjacent carbon atoms, and there is therefore no possibility of the formation of a five-membered ring, and so the action is the normal one. The constitution of muconic acid was discussed by Rupe, who concluded that it is correctly expressed by the formula $\text{CO}_2\text{H}\cdot\text{CH}:\text{CH}\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$; this conclusion is fully confirmed by the facts that the acid is obtained from $\alpha\delta$ -dibromoadipic acid and the ethyl ester from ethyl $\alpha\delta$ -dibromoadipate as described in the present communication.

In order to ascertain if cyclic compounds analogous to ethyl 1-phenylpyrrolidine-2:5-dicarboxylate would be obtained from the corresponding bromo-derivatives of other dicarboxylic acids, the action of aniline and monoethylaniline on these bromo-derivatives was investigated.

The action of aniline on ethyl $\alpha\beta$ -dibromosuccinate has been already studied by Gorodetzky and Hell (*Ber.*, 1888, 21, 1796), who obtained ethyl $\alpha\beta$ -dianilinosuccinate, $\text{CO}_2\text{Et}\cdot\text{CH}(\text{NHPh})\cdot\text{CH}(\text{NHPh})\cdot\text{CO}_2\text{Et}$, as the main product, together with a small quantity of a yellow compound which they were unable to identify. It was thought that this yellow substance might be the desired cyclic compound containing the ring

system $\text{C}_6\text{H}_5\cdot\text{N}<\begin{smallmatrix} \text{C} \\ | \\ \text{C} \end{smallmatrix}$, but this was found not to be the case, and

the compound was identified as the anil of anilinomaleic acid,



(Bischoff and Walden, *Annalen*, 1894, 279, 139).

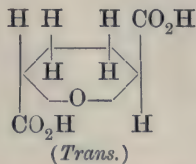
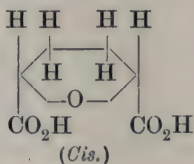
The action of monoethylaniline on ethyl $\alpha\beta$ -dibromosuccinate was next investigated, and in this case the compound obtained was ethyl bromomaleate, $\text{CO}_2\text{Et}\cdot\text{CBr}\cdot\text{CH}\cdot\text{CO}_2\text{Et}$, which was obtained in a 74.2 per cent. yield. Ethyl $\alpha\theta$ -dibromosebacate was then substituted for ethyl $\alpha\beta$ -dibromosuccinate, and heated with aniline, when it was found that no cyclic compound had been formed, but that the action had followed the normal course, and ethyl $\alpha\theta$ -dianilinosesbacate,



was obtained.

By heating an aqueous solution of the lactone of dihydroxybutane-

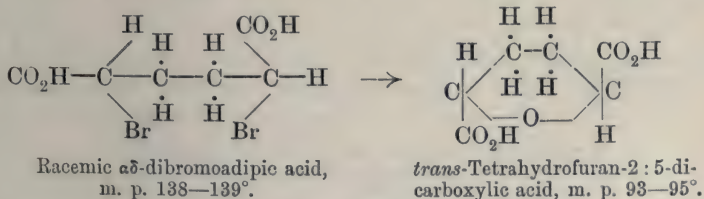
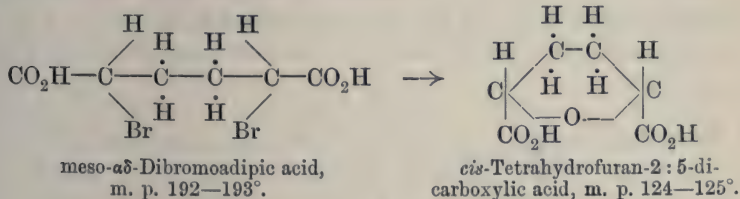
tetracarboxylic acid, Lean (Trans., 1900, **77**, 110) obtained two isomeric tetrahydrofuran-2 : 5-dicarboxylic acids, which he regarded as *cis*- and *trans*-modifications :



One of these acids melted at 123—125°, and the other, which melted at 93—95°, formed a hydrate melting at 63—64°, but Lean did not establish which of these acids was the *cis*- and which the *trans*-variety.

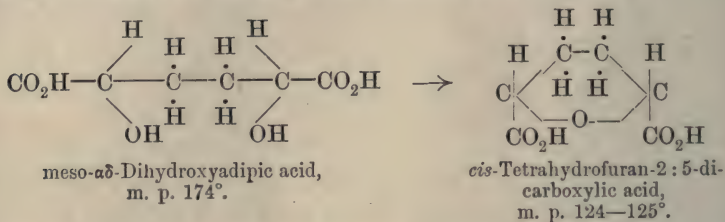
In a former communication (Le Sueur, Trans., 1908, **93**, 716), the preparation and identification of two $\alpha\delta$ -dihydroxyadipic acids were described, and it was shown that the $\alpha\delta$ -dihydroxyadipic acid melting at 174° is the meso-acid, and the one melting at 146° is the racemic variety. Corresponding with these two hydroxyadipic acids are two $\alpha\delta$ -dibromoadipic acids; of these, the one melting at 192—193° is the meso-acid, and the other, which melts at 138—139°, is the racemic acid (compare Rosenlew, Ber., 1904, **37**, 2090).

Now, when meso- $\alpha\delta$ -dibromoadipic acid is treated with alcoholic potash, the tetrahydrofuran-2 : 5-dicarboxylic acid obtained is the one melting at 124—125°, and from stereochemical considerations it will be seen that this must be the *cis*-variety :



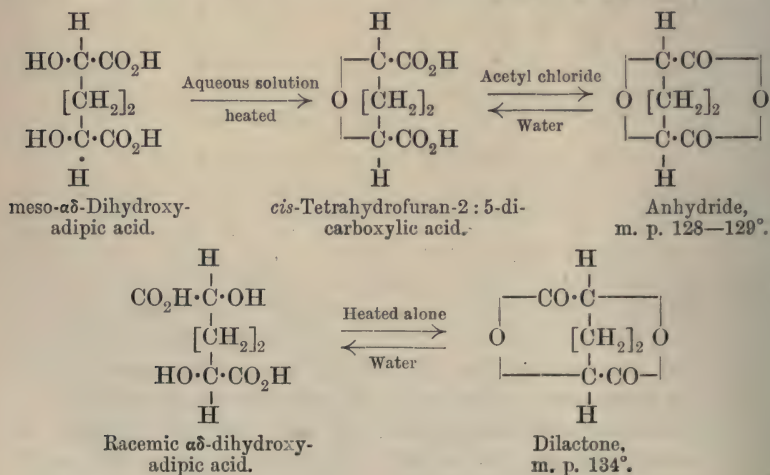
It might be argued that the meso-dibromoadipic acid under such severe treatment as the action of boiling alcoholic potash had undergone intramolecular change, and that the acid resulting from it was the *trans*- and not the *cis*-form. In order to settle this point,

an aqueous solution of the meso- $\alpha\delta$ -dihydroxyadipic acid was heated in a sealed tube, when the acid lost a molecule of water and gave the tetrahydrofuran-2:5-dicarboxylic acid melting at 124—125°:



Finally, if the furan acid melting at 124—125° is really the *cis*-acid, then it should form an anhydride, whereas the *trans*-acid would not. In order to investigate this point, the acid melting at 124—125° was boiled for several hours with an excess of acetyl chloride, when an anhydride, $\text{C}_6\text{H}_6\text{O}_4$, was obtained. This anhydride, on treatment with water, readily regenerated the acid melting at 124—125°, which proves conclusively that the acetyl chloride has not caused an intramolecular change, and that the anhydride really corresponds with the tetrahydrofuran-2:5-dicarboxylic acid melting at 124—125°, which latter acid must therefore be regarded as the *cis*-modification.

It is interesting to note that the above anhydride is isomeric with the dilactone obtained by heating racemic $\alpha\delta$ -dihydroxyadipic acid (Trans., 1908, 93, 721). Both the anhydride and the dilactone are formed by the loss of two molecules of water from their respective dihydroxyadipic acids, the former being formed in two stages: (1) the loss of a molecule of water from two hydroxyl groups; (2) the loss of



a second molecule of water from two carboxyl groups, whereas the dilactone is formed by the loss of two molecules of water, each molecule of water arising from one hydroxyl group and one carboxyl group.

EXPERIMENTAL.

Action of Diethylaniline on Ethyl α -Dibromoadipate.

Ten grams of ethyl α -dibromoadipate (m. p. 66°) and 16 grams of recently distilled diethylaniline were placed together in a flask attached to a reflux air condenser and containing a thermometer, the upper end of the condenser being connected to a U-tube immersed in a freezing mixture. The flask and contents were gradually heated to 190° , at which temperature the reaction began, and were maintained at 185 – 195° for three hours. During the heating a volatile liquid was evolved, and was condensed in the U-tube; the total amount of ester heated in this manner was 80 grams.

The volatile liquid, after being dried, weighed 15 grams, and boiled at 38 – 38.5° :

0.1544 gave 0.2644 AgBr. Br = 72.87.

C_2H_5Br requires Br = 73.39 per cent.

The liquid was therefore ethyl bromide, the boiling point of which is 38.37° .

The contents of the flask partly solidified on cooling, and were added to dilute hydrochloric acid and the whole extracted with ether; the ethereal solution was washed, dried, and evaporated, and the residue distilled under 29 mm. pressure:

165–185°	11.5 grams		230–255°	11.0 grams
210–228	3.0 „		Undistilled residue...	13.5 „

The fraction b. p. 165 – 185° slowly deposited long, flat crystals, which, after filtration and drying, weighed 3.3 grams, and, after crystallisation from light petroleum (b. p. 40 – 60°), melted at 63 – 64° , and consisted of ethyl muconate, the melting point of which is quoted as 63 – 64° by Ruhemann and Blackman (Trans., 1890, 57, 374):

0.1760 gave 0.3892 CO_2 and 0.1148 H_2O . C = 60.31; H = 7.24.

$C_{10}H_{14}O_4$ requires C = 60.60; H = 7.07 per cent.

The fraction b. p. 230 – 255° consisted for the most part of ethyl 1-phenylpyrrolidine-2:5-dicarboxylate, as was shown by the fact that it yielded 1-phenylpyrrolidine-2:5-dicarboxylic acid on hydrolysis with 10 per cent. alcoholic potash. The acid which was precipitated on acidifying the hydrolysed product with hydrochloric acid was crystallised from a mixture of acetone and light petroleum, from which it separated in oblong plates, which decomposed with evolution of gas at 249° . A mixture of equal parts of this substance and 1-phenyl-

pyrrolidine-2 : 5-dicarboxylic acid (Trans., 1909, 95, 277) decomposed at the same temperature :

0.1684 gave 8.6 c.c. N_2 (moist) at 13° and 764 mm. $N = 6.07$.

$C_{12}H_{13}O_4N$ requires $N = 5.96$ per cent.

The undistilled residue consisted of a dark thick syrup, which, after being kept for several months, showed no signs of solidifying, and from which no pure substance could be isolated.

Action of Aniline on Methyl $\alpha\delta$ -Dibromoadipate.

Eighteen grams of methyl $\alpha\delta$ -dibromoadipate and 18 grams of aniline were heated together in a flask immersed in boiling water for forty hours, and the product worked up and distilled as described under the action of diethylaniline on ethyl $\alpha\delta$ -dibromoadipate (p. 177). That portion of the distillate boiling at $225\text{--}230^\circ/32$ mm. weighed 8 grams, and solidified on cooling. It was crystallised from light petroleum, when it was obtained in needles, which melted at 88° and had all the properties of methyl 1-phenylpyrrolidine-2 : 5-dicarboxylate (Trans., 1909, 95, 277). A mixture of equal parts of these two substances melted at 88° . When hydrolysed by boiling with 10 per cent. alcoholic potash, it gave 1-phenylpyrrolidine-2 : 5-dicarboxylic acid, which decomposed and evolved gas at 252° .

Action of Monoethylaniline on Ethyl $\alpha\beta$ -Dibromosuccinate.

The ethyl dibromosuccinate was prepared by heating succinic acid with amorphous phosphorus and bromine in a sealed tube and esterifying the resulting bromo-acid with concentrated sulphuric acid and alcohol (Gorodetzky and Hell, *Ber.*, 1888, 21, 1729).

Twenty grams (1 mol.) of ethyl $\alpha\beta$ -dibromosuccinate and 15 grams (2 mols.) of monoethylaniline were heated together in boiling water for thirty-five hours ; the resulting product, which partly solidified on cooling, was extracted with much ether, and the insoluble residue of monoethylaniline hydrobromide filtered off. The ethereal filtrate was well washed with water, dried, and evaporated, and the residue distilled under 32 mm. pressure, when the whole distilled between 149° and 152° . It was re-distilled, and a portion boiling at $148\text{--}149^\circ$ collected for analysis :

0.2125 gave 0.2981 CO_2 and 0.0838 H_2O . $C = 38.26$; $H = 4.38$.

0.1854 „ 0.1400 AgBr. $Br = 32.13$.

$C_8H_{11}O_4Br$ requires $C = 38.24$; $H = 4.38$; $Br = 31.87$ per cent.

The above substance is therefore ethyl monobromomaleate, the boiling point of which is given as $143^\circ/30\text{--}40$ mm. (Anschütz, *Ber.*, 1879, 12, 2284).

Twenty grams of ethyl dibromosuccinate gave 11.2 grams of the pure ester, which corresponds with 74.2 per cent. of the theoretical, so that this reaction affords a very convenient method for preparing ethyl monobromomaleate.

The interaction of monoethylaniline and ethyl $\alpha\beta$ -dibromosuccinate was tried under various conditions, such as heating together the two substances in alcoholic solution; heating together at 180—200°, but in all cases ethyl monobromomaleate was the only substance obtained.

Action of Aniline on Ethyl $\alpha\beta$ -Dibromosuccinate.

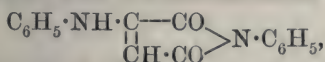
Ten grams of ethyl $\alpha\beta$ -dibromosuccinate (1 mol.) and 14 grams (5 mols.) of aniline were heated together for two hours in a flask immersed in boiling water. The contents of the flask partly solidified on cooling, and were treated with a large volume of ether and the crystalline solid collected. This solid, which consisted chiefly of aniline hydrobromide, was treated with 80 c.c. of warm water, the solution cooled, and the undissolved residue (0.8 gram) collected and crystallised from alcohol, when it was obtained in glistening needles, which melted at 149° and had all the properties of ethyl $\alpha\beta$ -dianilinosuccinate, the melting point of which is given as 150° by Gorodetzky and Hell (*Ber.*, 1888, **21**, 1797).

The ethereal filtrate, on evaporation, left a residue which showed signs of decomposition on attempting to distil it under diminished pressure; it was therefore not distilled, but alcohol was added to it when a yellow solid slowly separated. This solid was repeatedly crystallised, first from acetone and finally from a mixture of chloroform and light petroleum, when it was obtained in small needles melting at 230°:

0.1224 gave 10.8 c.c. N_2 (moist) at 18.5° and 769 mm. $N = 10.29$.

$C_{16}H_{12}O_2N_2$ requires $N = 10.60$ per cent.

This yellow solid is insoluble in ether, light petroleum, or alcohol, and moderately soluble in boiling chloroform or acetone; it is therefore identical with the anilinomaleic anil,



obtained by Bischoff and Walden (*loc. cit.*).

The yield of the above yellow solid was very small, and many attempts were made to increase it, but without any substantial improvement. Among these attempts may be mentioned: (1) addition of anhydrous sodium acetate to the mixture of ester and aniline; (2) the substitution of aniline hydrochloride for aniline; (3) the

interaction of the ester and aniline in alcoholic solution in the cold; (4) the interaction of the ester and aniline in the presence of potassium hydroxide; (5) heating the ester and aniline at 190° .

Action of Aniline on Ethyl $\alpha\theta$ -Dibromosebacate.

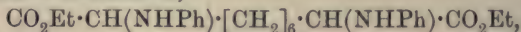
The ethyl $\alpha\theta$ -dibromosebacate was prepared by the action of bromine on the acid chloride of sebacic acid, and esterification of the resulting bromo-acid chloride by the interaction of this substance and alcohol.

Twenty grams (1 mol.) of ethyl $\alpha\theta$ -dibromosebacate and 20 grams (4 mols.) of recently distilled aniline were heated together for eleven hours in a flask immersed in boiling water. The resulting solid was triturated with dilute hydrochloric acid, and the undissolved solid (4.5 grams) collected and washed with water. The hydrochloric acid solution was diluted with a large volume of water, when a solid was precipitated; the whole was extracted with ether, the ethereal solution washed, dried, and evaporated, when 12.5 grams of solid residue were obtained. This was added to the above 4.5 grams of undissolved residue, and recrystallised from alcohol until the melting point was constant:

0.1304 gave 7.5 c.c. N_2 (moist) at 18.5° and 756 mm. $N = 6.58$.

$C_{26}H_{36}O_4N_2$ requires $N = 6.36$ per cent.

Ethyl $\alpha\theta$ -dianilino-sebacate,



melts at 119.5 — 120.5° , and crystallises from alcohol in fern-like aggregates. It is insoluble in water, sparingly soluble in ether, alcohol, or light petroleum, and readily so in chloroform, benzene, or acetone.

The alcoholic mother liquors from which the above ester had crystallised gave a substance which, after recrystallisation, melted at 94 — 100° , and on analysis gave the following results:

0.1680 gave 0.4378 CO_2 and 0.1342 H_2O . $C = 71.07$; $H = 8.87$.

0.1734 „ 9.7 c.c. N_2 (moist) at 16° and 764 mm. $N = 6.55$.

$C_{26}H_{36}O_4N_2$ requires $C = 70.90$; $H = 8.18$; $N = 6.36$ per cent.

This substance is therefore in all probability stereoisomeric with the ethyl $\alpha\theta$ -dianilino-sebacate melting at 119.5 — 120.5° , but repeated recrystallisation failed to give a substance with a definite melting point.

$\alpha\theta$ -Dianilino-sebacic Acid.—Thirty-three grams of ethyl $\alpha\theta$ -dianilino-sebacate were added to a solution of 20 grams of potassium hydroxide in 150 c.c. of alcohol containing a few c.c. of water, and the whole boiled for five hours. The resulting solution was concentrated to half its volume, and gradually added to a boiling solution of 25 c.c. con-

concentrated sulphuric acid in 125 c.c. of water, when the anilino-acid was precipitated in a granular form. If the precipitation is carried out in the cold, then the acid separates in an amorphous form, in which condition it is difficult to manipulate. The acid was collected, washed with water, dried, and boiled with 80 c.c. of alcohol in order to remove any non-hydrolysed ester, filtered, and after drying weighed 23 grams. It was crystallised from amyl alcohol, from which it separated in spherical aggregates of small needles, which melt and evolve gas at 210—213° :

0.1254 gave 0.3180 CO₂ and 0.0868 H₂O. C = 69.15 ; H = 7.69.

0.1707 „ 10.6 c.c. N₂ (moist) at 18° and 765 mm. N = 7.21.

C₂₂H₂₈O₄N₂ requires C = 68.75 ; H = 7.29 ; N = 7.29 per cent.

αβ-Dianilino-sebacic acid,



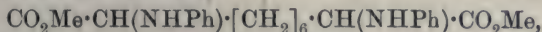
is insoluble in water, alcohol, ether, chloroform, light petroleum, benzene, or ethyl acetate, and only sparingly soluble in boiling amyl alcohol.

The *silver* salt was obtained as a white precipitate on adding a solution of the sodium salt of the acid to a solution of silver nitrate ; it darkened somewhat readily on drying :

0.1510 gave 0.0536 Ag. Ag = 35.5.

C₂₂H₂₆O₄N₂Ag₂ requires Ag = 36.1 per cent.

Methyl αβ-dianilino-sebacate,



was prepared by the interaction of aniline and methyl *αβ*-dibromo-sebacate, as described for the preparation of the corresponding ethyl ester. It is insoluble in water, ether, or light petroleum, readily soluble in benzene or chloroform, and crystallises from alcohol, in which it is sparingly soluble, in fern-like aggregates of needles melting at 133—136° :

0.1334 gave 7.9 c.c. N₂ (moist) at 19° and 768 mm. N = 6.88.

C₂₄H₃₂O₄N₂ requires N = 6.79 per cent.

Action of Alcoholic Potassium Hydroxide on meso-αδ-Dibromoadipic Acid.

The *meso-αδ*-dibromoadipic acid was separated from the mixture of racemic and *meso-αδ*-dibromoadipic acids obtained by the action of bromine on the acid chloride of adipic acid (Trans., 1908, **93**, 718) by extracting the mixed acids with water and crystallising the insoluble residue of the *meso*-acid from formic acid until its melting point was constant (Rosenlew, *Ber.*, 1904, **37**, 2090).

Seven and a-half grams of *meso-αδ*-dibromoadipic acid (m. p.

192—193°) were dissolved in 15 c.c. of hot alcohol, and the hot solution gradually added to a boiling solution of 10.5 grams of potassium hydroxide in 60 c.c. of alcohol. A vigorous reaction immediately set in, and the mixture was boiled on the water-bath for fifteen minutes, then allowed to cool, and filtered (filtrate = A). The insoluble residue was dissolved in 15 c.c. of water, the solution strongly acidified with concentrated hydrochloric acid, and, after some time, a crystalline precipitate separated; this was collected and dissolved in dilute potassium hydroxide solution, and again precipitated by hydrochloric acid, when it was obtained in a crystalline form. The substance had all the properties of muconic acid, and decomposed without melting at 272°:

0.1608 gave 0.2966 CO₂ and 0.0678 H₂O. C = 50.30; H = 4.68.

C₆H₆O₄ requires C = 50.70; H = 4.22 per cent.

The aqueous filtrate from the muconic acid was evaporated to a small bulk, and repeatedly extracted with a large volume of ether. The ethereal solution was evaporated without previous washing or drying, and the residue dried and crystallised from a mixture of ethyl acetate and light petroleum, when it was obtained in nodular aggregates melting at 124—125°:

0.1434 gave 0.2344 CO₂ and 0.0684 H₂O. C = 44.58; H = 5.30.

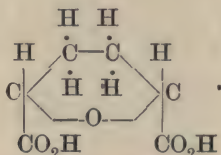
C₆H₈O₅ requires C = 45.00; H = 5.00 per cent.

The molecular weight was determined by dissolving the acid in water and titrating with *N*/10-sodium hydroxide, using phenolphthalein as indicator:

0.2040 required 25.6 c.c. *N*/10-NaOH, which corresponds with a dibasic acid of M.W. = 159.4.

A dibasic acid, C₆H₈O₅, requires M.W. = 160.

The substance is therefore *cis*-tetrahydrofuran-2:5-dicarboxylic acid,



It readily chars when heated above its melting point, and its solubilities in various solvents correspond exactly with those of the tetrahydrofuran-2:5-dicarboxylic acid melting at 123—125° obtained by Lean (*loc. cit.*).

The alcoholic filtrate A (see above) was saturated with carbon dioxide, and the precipitated potassium hydrogen carbonate collected. The filtrate was evaporated to dryness, the residue dissolved in a very

small quantity of water, and the resulting solution acidified with hydrochloric acid and repeatedly extracted with a large volume of ether. The ethereal solution on evaporation left a small residue, which, after crystallisation from ethyl acetate and light petroleum, melted at 174° and had all the properties of meso- $\alpha\delta$ -dihydroxyadipic acid (Trans., 1908, 93, 723).

The aqueous mother liquors from the ether extracts were mixed and evaporated to dryness; the residue obtained was dried, extracted with alcohol, and the alcoholic solution evaporated and the residue crystallised from ethyl acetate and light petroleum, when a further small quantity of the tetrahydrofuran acid melting at 124 – 125° was obtained.

The amount of tetrahydrofuran acid obtained corresponded with 28 per cent. of the theoretical, and the yield of muconic acid was only 14 per cent. of the theoretical.

The *ammonium* salt was prepared by dissolving the acid in alcohol and saturating the solution with ammonia, when the salt was precipitated; it was collected, and crystallised by dissolving in a small quantity of water and adding alcohol and ether, when it separated out in long, transparent prisms. It is readily soluble in water, sparingly so in alcohol, and insoluble in ether:

0.1231, boiled with NaOH, gave 0.0213 NH_3 . $\text{N} = 14.24$.

$\text{C}_6\text{H}_6\text{O}_5(\text{NH}_4)_2$ requires $\text{N} = 14.43$ per cent.

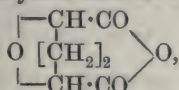
Anhydride of cis-Tetrahydrofuran-2 : 5-dicarboxylic Acid.

Twenty grams of acetyl chloride and 2.8 grams of *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid were boiled together for sixteen hours in a flask attached to a reflux condenser. The acetyl chloride was removed by evaporation in a vacuum over 50 per cent. potassium hydroxide solution, and the resulting solid spread on a porous plate, when 2.5 grams of solid, melting at 97 – 105° , were obtained. This, on extraction with 15 c.c. of dry chloroform, left 1.5 grams of residue which melted at 122° , and consisted of the unchanged acid. The chloroform extract, on evaporation in a vacuum, gave 0.6 gram of a solid, which was crystallised from dry chloroform and light petroleum, when it was obtained in slender needles:

0.1022 gave 0.1876 CO_2 and 0.0414 H_2O . $\text{C} = 50.1$; $\text{H} = 4.5$.

$\text{C}_6\text{H}_6\text{O}_4$ requires $\text{C} = 50.7$; $\text{H} = 4.2$ per cent.

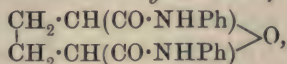
The *anhydride* of *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid,



readily volatilises when heated, even on the water-bath, and yields a

sublimate of long needles, which melt at 128—129°. It is readily soluble in ethyl acetate, chloroform, ether, or acetone in the cold, and is insoluble in light petroleum. It slowly dissolves in cold water, giving a strongly acid solution, which on evaporation gives the original *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid melting at 124—125°. When the anhydride is heated with resorcinol and a few drops of sulphuric acid, and the product poured into a solution of potassium hydroxide, a green, fluorescent solution is obtained.

cis-Tetrahydrofuran-2 : 5-dicarboxyldianilide,



was prepared by boiling the acid (0.2 gram) with a large excess of aniline (2 grams) for seven hours. The product was poured into dilute hydrochloric acid, and the precipitated solid collected, dissolved in alcohol, and the solution decolorised by animal charcoal. The solid which separated out on cooling was crystallised from alcohol, when it was obtained in small, thick plates, melting and decomposing at 208—209°. The dianilide is readily soluble in acetone or chloroform in the cold, sparingly soluble in hot benzene or cold alcohol, and insoluble in water :

0.1176 gave 9.4 c.c. N_2 (moist) at 12° and 766 mm. $\text{N} = 9.51$.

$\text{C}_{18}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{N} = 9.03$ per cent.

Formation of cis-Tetrahydrofuran-2 : 5-dicarboxylic Acid from meso-αδ-Dihydroxyadipic Acid.

One gram of meso-αδ-dihydroxyadipic acid (m. p. 174°), obtained by hydrolysis of the meso-αδ-dibromoadipic acid melting at 192—193° (Trans., 1908, 93, 719), was dissolved in 5 c.c. of water, and the solution heated in a sealed tube for three hours at 200°. The solution was filtered to remove a small quantity of black solid, and the filtrate repeatedly extracted with a large volume of ether. The ethereal solution on evaporation left 0.2 gram of solid which, after drying and crystallisation from ethyl acetate and light petroleum, melted at 124—125°; this melting point was unaltered by mixing the substance with an equal quantity of *cis*-tetrahydrofuran-2 : 5-dicarboxylic acid. The substance readily charred when heated above its melting point, and its solubilities in various solvents were identical with those of the *cis*-furan acid.

Action of Alcoholic Potassium Hydroxide on Racemic αδ-Dibromoadipic Acid

The action of alcoholic potassium hydroxide on the racemic αδ-dibromoadipic acid (m. p. 138—139°) was investigated in the hope

of obtaining the *trans*-tetrahydrofuran-2:5-dicarboxylic acid. The method of procedure was exactly as described for the action of alcoholic potassium hydroxide on the meso-dibromoadipic acid, and muconic acid and a trace of the *cis*-tetrahydrofuran acid were obtained, together with a small quantity of residue which could not be crystallised. No such residue was obtained from the action of alcoholic potassium hydroxide on the meso-dibromoadipic acid, and it is not improbable that this residue did contain some of the *trans*-tetrahydrofuran acid, which, on account of its solubility and reluctance to crystallise (Lean, *loc. cit.*), could not be isolated.

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XIX.—*The Half-life Period of Radium; a Correction.*

By ROBERT WHYTLAW GRAY and SIR WILLIAM RAMSAY, K.C.B.

IN making the calculation of the half-life period of radium in the paper which has recently appeared (Trans., 1909, 95, 1082), an error, which Mr. Soddy was so good as to point out to us, was made inadvertently. Half the reciprocal of the disintegration-constant of radium, equal to half the average life-period, was given as the period of half-decay, namely, 1258 years. The true half-life period should have been calculated from the equation: $R = R_0 e^{-\Lambda t}$, where R is the initial amount of radium, R_0 the quantity remaining after half has decayed, e the base of natural logarithms, Λ the disintegration-constant for radium (the reciprocal of which is the average life-period), and t the time in years.

To find Λ from the equilibrium-quantity, N_0 , of emanation per gram of radium, the volume of which was 0.601 cub. mm., the amount of emanation given off per second was calculated by means of the equation: $q_0 = \lambda N_0 = \frac{0.601}{481,000} = 1.25 \times 10^{-6}$ cubic millimetres per second; the fraction $1/481,000$ is the value of λ , the disintegration constant for the emanation, calculated from the half-life period of 3.86 days. This volume is equal to the diminution in volume of 1 gram of radium per second, supposing it to be a monatomic gas.

Hence the fraction of the total quantity of radium changed per second is 1.25×10^{-6} of the volume of 1 gram of gaseous radium.

This is equal to $\frac{1.25 \times 10^{-6} \times 226}{22,400 \times 1000}$, 226 being the accepted atomic

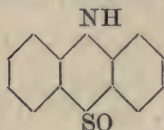
weight for radium; the expression is equivalent to $1/2516$ per year, and is Λ , or the disintegration-constant for radium. In decimals, it is 3.98×10^{-4} gram per year; hence the half-life period for radium is 1744 years, or, in other words, 1 gram of radium will have been reduced to 0.5 gram after 1744 years.

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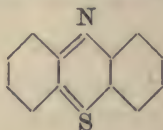
XX.—*The Intramolecular Rearrangement of Diphenylamine ortho-Sulphoxides. Part II.*

By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

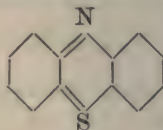
IN a previous communication to the Society on this subject it was shown that the ortho-sulphoxides of diphenylamine (type I) may be transformed by the action of acid reagents into the sulphonium hydrates (type II). At the same time it was observed that if the



(I.)



(II.)



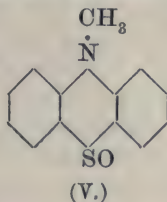
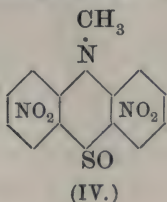
(III.)

sulphonium grouping be sufficiently basic, the corresponding salt (type III) may be formed. The tetranitro- and the two isomeric dinitro-sulphoxides yielded the sulphonium hydrates, but the parent compound (I) furnished phenazothionium chloride. In the four cases examined, it was observed that the sulphonium derivatives contain an additional molecule of water; but usually this may be removed by crystallisation from high boiling solvents.

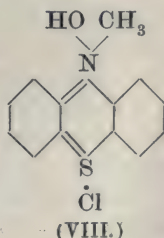
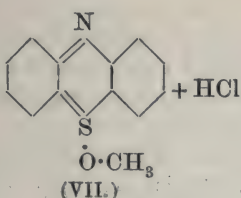
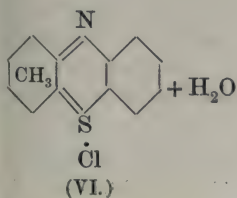
The investigation of this reaction has been continued with the object of determining the mechanism by which the change takes place, and the results are now collected in the following pages.

From the mere inspection of the formulæ (I and II) representing the initial and final products of the reaction, it might be supposed that the sulphonium hydrate is formed simply by the migration of hydrogen from the imino-group to the oxygen of the thionyl group. In order to test whether this is actually the case or not, we have examined the behaviour of sulphoxides in which this iminic hydrogen is replaced by alkyl. It has been found that these derivatives undergo the change as readily as the unsubstituted compounds. The two chief examples studied were the dinitro-*N*-methyldiphenylamine ortho-sulphoxide (IV), which has been pre-

viously obtained by Bernthsen from the nitration of *N*-methylthiodiphenylamine, and the *N*-methyldiphenylamine sulphoxide (V), which we have prepared by oxidation of the sulphide.



Assuming that the course of the reaction is the same with these *N*-alkyl derivatives as with the imino-compounds, it might then be concluded that with the latter the reaction does not involve the direct movement of the imino-hydrogen atom, for on a priori grounds it is improbable that the alkyl group should be transferred with such ease under the conditions favourable to the reaction. This conclusion, however, cannot be accepted until some actual proof is obtained of the immobility of the alkyl group, for many instances are known where the transposition of alkyl from one atom to another can be detected, although the treatment then required is usually more energetic than that necessary to the present reaction. The proof that alkyl is not removed from nitrogen during the reaction has been obtained in the case of *N*-methyldiphenylamine *o*-sulphoxide. This sulphoxide, when treated with hydrogen chloride, absorbs one molecular proportion of the halogen acid, being then converted into the chloride of a base which is deep red in colour and has properties similar to those of the phenazothionium derivatives described in a previous paper. It may be remarked that the quinonoid structure of this chloride is demonstrated by the further action of hydrochloric acid, which yields a chloro-derivative of *N*-methylthiodiphenylamine. If the methyl group is transferred from the nitrogen in this reaction, the only alternatives are that it may either enter the aromatic nucleus (as in VI), or become attached to the thionyl group (as in VII). In either case the substance which is formed would be represented as follows (VI and VII):



and on reduction it should furnish either a methylthiodiphenylamine (from VI) or thiodiphenylamine itself (from VII). We find, however, that reduction of the quinonoid salt does not yield either of these compounds, but that instead *N*-methylthiodiphenylamine is formed. It follows that the constitution of this substance must be as represented in the third of the foregoing (VIII) formulæ; but it is impossible conclusively to show whether salt formation takes place at the ammonium or sulphonium groups. Moreover, the salt is not very stable, since, as previously noticed, it readily changes to chloro-*N*-methylthiodiphenylamine, thus affording further proof of the immobility of the methyl group. The experiments dealing with these derivatives of *N*-methylthiodiphenylamine are described in the following paragraphs.

EXPERIMENTAL

Conversion of N-Methyldiphenylamine ortho-Sulphoxide into the Sulphonium Derivative.

Attempts to prepare this sulphoxide were made by treating *N*-methylthiodiphenylamine with hydrogen dioxide in acetone solution, but only small quantities of the substance could be obtained by this method, almost the whole of the sulphide being recovered unchanged after remaining with the reagent for about three weeks. Attention is drawn to this result, since thiodiphenylamine is readily oxidised to the sulphoxide under these conditions. Bernthsen (*Annalen*, 1885, **230**, 92) has shown that *N*-methylthiodiphenylamine may be converted into the sulphone by hot aqueous permanganate, but we find that this reagent under similar conditions furnishes satisfactory yields of the sulphoxide.

A solution of six grams of *N*-methylthiodiphenylamine in acetone was acidified with dilute sulphuric acid, more acetone being added, if necessary, to retain all in solution. Two grams of finely powdered potassium permanganate were then gradually added, the temperature being kept at about 15° by immersing the flask in cold water. Care was taken to ensure the presence of a slight excess of sulphuric acid during the reaction. The mixture was shaken for a few hours; then the crystalline precipitate was collected, and well washed with water. The residue was agitated with a cold aqueous solution of sulphurous acid, and finally recrystallised from alcohol. The least soluble portion contained small quantities of the sulphone, and it was therefore rejected. Nine grams of the crude sulphoxide were obtained from 18 of sulphide.

N-Methyldiphenylamine ortho-sulphoxide forms colourless leaflets, which melt at 193°. It is sparingly soluble in cold acetone or

alcohol, and insoluble in water. Concentrated sulphuric or hydrochloric acid forms bright red solutions, which contain the phenazothionium derivative. A sample which had been dried in a vacuum was analysed:

0.1009 gave 0.2520 CO_2 and 0.0443 H_2O . $\text{C} = 67.9$; $\text{H} = 4.88$.

0.2315 „, 12.6 c.c. N_2 at 17° and 763 mm. $\text{N} = 6.4$.

$\text{C}_{13}\text{H}_{11}\text{ONS}$ requires $\text{C} = 68.1$; $\text{H} = 4.8$; $\text{N} = 6.3$ per cent.

Action of Acids.—This sulphoxide is readily soluble in concentrated aqueous hydrochloric acid, being then converted into the deep crimson hydrochloride. The attempts made to isolate the latter in the pure condition were unsuccessful, chiefly on account of the hygroscopic nature of the substance, and the ease with which it is transformed into the chloro-derivative of *N*-methylthiodiphenylamine. The platinichloride was therefore prepared by addition of chloroplatinic acid to the aqueous solution of the salt. The precipitate was collected, and after recrystallisation it was dried in a vacuum before analysis:

0.2161 gave 0.0474 Pt. $\text{Pt} = 21.93$.

0.1184 „, 0.1568 CO_2 and 0.0238 H_2O . $\text{C} = 36.1$; $\text{H} = 2.2$.

$(\text{C}_{13}\text{H}_{11}\text{ONS}, \text{HCl})_2\text{PtCl}_4$ requires $\text{Pt} = 22.4$; $\text{C} = 35.9$.

$\text{H} = 2.7$ per cent.

The *platinichloride* of *N*-methylphenazothionium (VIII) forms minute, reddish-brown needles, which melt with profound decomposition at about 255° .

Reduction.—The hydrochloride was reduced as rapidly as possible in methyl-alcoholic solution with tin and hydrochloric acid. When reduction was complete, the colourless solution was poured into water, and the precipitate was collected. The product contained a small quantity of the chloro-derivative, and, in order to remove this, it was fractionally crystallised from methyl alcohol. The melting point and solubility of the chloro-compound lie close to those of *N*-methylthiodiphenylamine, and a complete separation is not easily made. However, after repeated crystallisation, a sample, which melted at 98° , was obtained, and this, when mixed with *N*-methylthiodiphenylamine (m. p. 100°), melted at the same temperature. It contained traces of chlorine. In order to obtain further proof that thiodiphenylamine is not formed during the reduction of the chloride, both the crude and purified (m. p. 98°) products of reduction were treated with nitric acid (D 1.4) under the conditions which yield the dinitro-derivatives of the group. The nitro-derivative was insoluble in hot aqueous alkali hydroxide, whereas the nitro-derivatives of thiodiphenylamine are readily attacked by this reagent, yielding deep red solutions of the alkali

salts. Experiments made with artificial mixtures showed that very small quantities of thiodiphenylamine may be detected in the presence of a large excess of the *N*-methyl derivative by this method. These experiments show that the methyl group of *N*-methylthiodiphenylamine remains undisturbed during the conversion to the quinonoid salt.

Conversion of N-Methyldinitrophenylamine o-Sulphoxide.—The dinitro-sulphoxide was prepared from *N*-methylthiodiphenylamine by the action of nitric acid, and it was purified in the manner recommended by Bernthsen (*Annalen*, 1885, **230**, 92). To ensure the purity of the substance employed, a sample was analysed:

0.1037 gave 0.1841 CO_2 and 0.0298 H_2O . $\text{C} = 48.4$; $\text{H} = 3.2$.

$\text{C}_{13}\text{H}_9\text{O}_5\text{N}_3\text{S}$ requires $\text{C} = 48.9$; $\text{H} = 2.8$ per cent.

The conversion of the sulphoxide into the sulphonium derivative was effected by means of sulphuric or hydrochloric acid.

(a) *Concentrated Sulphuric Acid.*—A solution of dinitro-*N*-methyldiphenylamine *o*-sulphoxide in this acid was set aside for half an hour at the atmospheric temperature, and then poured on to powdered ice. The solid precipitate was collected and washed with water until free from sulphuric acid; it was then triturated with dilute aqueous sodium hydroxide to remove a small quantity of soluble material. The latter is probably formed by replacement of the nitro- by the hydroxyl group (see Barnett and Smiles, *Trans.*, 1909, **95**, 1262), but it was not further investigated. After renewed filtration and washing, the reddish-brown product was crystallised from hot glacial acetic acid. Samples of the once (1) and four times recrystallised (2) product were analysed after being dried in the steam-oven.

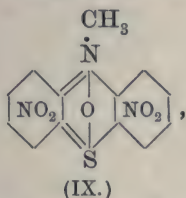
(b) *Hydrogen Chloride.*—Methyl alcohol was saturated with gaseous hydrogen chloride at 0° , and excess of the solution was mixed with the dinitro-sulphoxide. The mixture was shaken for six hours, and then set aside at the atmospheric temperature. After the lapse of forty-eight hours, the dark brown liquid contained in suspension an orange-red, crystalline substance, and, since this evidently was different from the more soluble portion, it was collected and separately treated. The solution, which was shown by subsequent experiment to contain the bulk of the desired sulphonium compound, was mixed with a large quantity of water, and the now insoluble product was collected and purified by recrystallisation from glacial acetic acid. Analysis (3) was then made with a sample from the fourth recrystallisation. The crude product contained traces of non-ionisable halogen:

- (1) 0.1010 gave 0.1774 CO₂ and 0.0296 H₂O. C=47.9; H=3.26.
 (2) 0.1005 „ 0.1752 CO₂ „ 0.0260 H₂O. C=47.5; H=2.87.
 (3) 0.1006 „ 0.1752 CO₂ „ 0.0287 H₂O. C=47.5; H=3.16.

C₁₃H₉O₅N₃S_{1/2}H₂O requires C=47.56; H=3.0 per cent.

The analyses show that, as with the nitro-derivatives of thio-diphenylamine which have been previously studied (Trans., 1909, 95, 1257), the conversion of the sulphoxide to the sulphonium derivative is accompanied by absorption of water; but here the molecular proportion is half that previously observed, and it is more firmly retained, since it cannot be removed by heating or by recrystallisation from high boiling solvents.

Dinitro-N-methylphenazothionium hydrate forms reddish-brown leaflets, which do not melt below 250°. It is sparingly soluble in cold benzene or glacial acetic acid. By reduction and subsequent oxidation, the substance is converted into the greenish-blue dye which is obtained by the same process from the dinitro-sulphoxide; but in contrast with the latter it does not exhibit the reaction characteristic of the thionyl group (Trans., 1906, 89, 696), since it does not yield the *S*-phenetyl derivative when treated with phenetole and sulphuric acid. The only formula which can be assigned to the anhydrous compound is the following:



but from reasons which will presently be stated, it is probable that the additional water in these substances is of constitution.

The insoluble portion of the product which was obtained by the action of hydrochloric acid on the dinitro-sulphoxide was separately collected and recrystallised from hot glacial acetic acid. It was thus obtained in bright orange-red leaflets, which remained undecomposed at 250°. Samples from two different preparations were analysed:

- (1) 0.1004 gave 0.1777 CO₂ and 0.0303 H₂O. C=48.3; H=3.51.
 (2) 0.2028 „ 0.3616 CO₂ „ 0.0516 H₂O. C=48.6; H=2.8.

C₁₃H₉O₅N₃S requires C=48.90; H=2.82 per cent.

When crystallised from hot nitrobenzene, the substance is obtained with solvent of crystallisation:

0.2000 gave 0.3718 CO₂ and 0.0656 H₂O. C=50.7; H=3.6.

2C₁₃H₉O₅N₃S.C₆H₅O₂N requires C=50.6; H=3.0 per cent.

The presence of nitrobenzene in this substance was proved by mixing the sulphuric acid solution with water and passing a current of steam through the liquid. The substance melts and decomposes at about 280°. Further experiment showed that this compound does not contain the sulphonium grouping, and since it yields the *S*-phenetylsulphonium salt when treated with phenetole in sulphuric acid solution, it may for the present be regarded as an isomeric form of the original sulphoxide. Probably the isomerism involves the nitro-grouping.

Assuming that the conversion of sulphoxide (I) to sulphonium base (II) takes place in the same manner with the imino-compounds as with these *N*-methyl derivatives, it is clear that the hypothesis of migration of hydrogen from the imino- to the thionyl group cannot be accepted as an adequate explanation of the change. The ortho-sulphoxides of diphenylamine contain the imino- and thionyl groups, and it is well known that each of these in simple derivatives possesses basic properties. So far as the thionyl group is concerned, it has been shown that the aliphatic (Saytzeff, *Annalen*, 1867, **144**, 148) and aromatic (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 697) sulphoxides form nitrates and hydrochlorides. From these considerations and from the fact that the reaction can be effected only by acid reagents, it seems probable that the salts of the sulphoxides are formed in an initial stage of the reaction, and that these are subsequently changed into the sulphonium derivatives. That a causal relation exists between the formation of these salts and the production of the sulphonium compounds may be shown by the following experiments.

(1) *The Action of the same Acid Reagent on Sulphoxides of Varying Basic Power.*—Experiments were made with the tetra-nitro-, di-*p*-nitro-, *isodinitro*-, and the unsubstituted diphenylamine sulphoxides, the reagent being alcohol saturated with hydrogen chloride at the atmospheric temperature. In each case the conditions adopted were the same: the sulphoxide was shaken with a large excess of the acid reagent at about 15–17°, and the approximate time required for the complete conversion to the sulphoxide was observed. The results are collected in the following table:

Substance.	Approximate time required.
Diphenylamine <i>o</i> -sulphoxide.....	apparently instantaneous.
<i>N</i> -Methyldiphenylamine <i>o</i> -sulphoxide.....	apparently instantaneous.
Di- <i>p</i> -nitrodiphenylamine <i>o</i> -sulphoxide.....	about five hours.
<i>iso</i> Dinitrodiphenylamine <i>o</i> -sulphoxide.....	about five hours.
Tetranitrodiphenylamine <i>o</i> -sulphoxide ...	about three weeks.

The data cannot be regarded as anything more than very rough approximations; but they serve to show that by decreasing the

basic function of the sulphoxides, the tendency to form the sulphonium base is correspondingly diminished.

(2) *The Action of Acids of Varying Strength on the same Sulphoxide.*—In these experiments the diphenylamine *o*-sulphoxide was employed as the standard. The colourless solutions of this substance become deeply coloured on the addition of acids, the salt of phenazothionium being then formed. Equal volumes (50 c.c.) of 2*N*-aqueous solutions of acetic, monochloroacetic, trichloroacetic, and hydrochloric acids were separately mixed at the same moment with 50 c.c. of an alcoholic solution (0.1 per cent.) of the sulphoxide. After a suitable lapse of time (thirty minutes), the solutions were examined in layers of equal depth. A difference between the intensity of colour in these solutions could be readily detected, but quantitative measurements of the intensity were not made, since the solutions containing the stronger acids were of slightly different colour, probably owing to the formation of di-acid salts. When arranged in order of increasing intensity of colour, the solutions fall into the following order:

Fifty c.c. of 0.1 per cent. Solution of Diphenylamine Sulphoxide in Alcohol.

With 50 c.c. of 2 <i>N</i> -solution of	Relative coefficients of saponification velocity.	Remarks.
Acetic acid	0.003	colour appeared after 1 hour.
Monochloroacetic acid	0.043	faint colour immediately produced.
Trichloroacetic acid	0.682	immediate coloration.
Hydrochloric acid	1.000	immediate coloration.

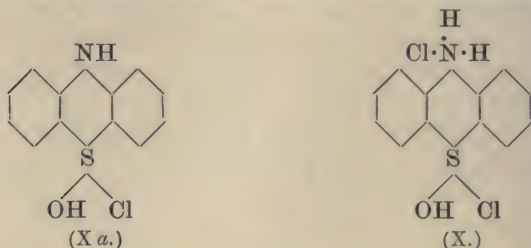
It may be remarked that after the further lapse of time the intensity of colour in these solutions increases, and the difference between each solution becomes even more pronounced. The centre column of the table shows the relative affinities of the acids; the data were obtained by Ostwald (*J. pr. Chem.*, 1883, [ii], 28, 449) from measurements of the velocity of hydrolysis of methyl acetate.

Assuming that the intensity of colour of these solutions is roughly proportionate to the quantity of azothionium salt present, it follows that the amount of this salt formed at the end of a given period is controlled by the strength of the acid employed. It is clear that these two sets of experiments justify the hypothesis that the conversion of the sulphoxides to the sulphonium compounds depends on the preliminary formation of salts of the former substances with the acid reagent.

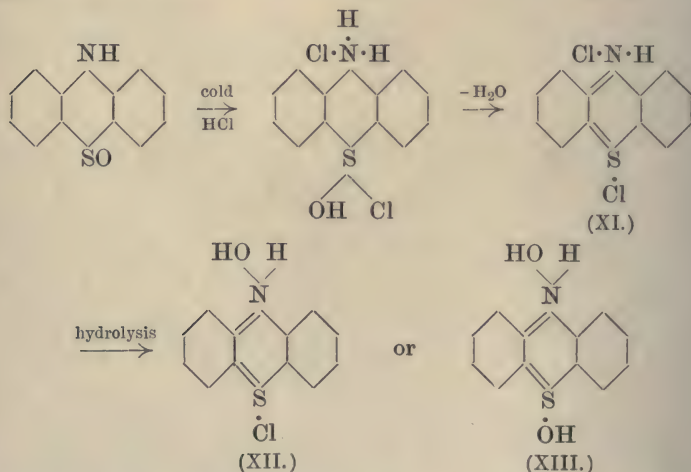
It is, however, difficult conclusively to determine the process by which these salts are converted to the quinonoid compounds, since they cannot be isolated in the pure condition for separate treat-

ment. There are, however, only two alternatives: either (a) that they lose the elements of water, or (b) that migration of hydroxyl takes place. These will be separately dealt with in the order given.

To assume that elimination of water takes place in the mono-acid sulphonium salt (Xa) is evidently incorrect, for on this basis the conversion of the *N*-methyl derivative would be impossible, and no account would be forthcoming of the additional molecule of water in the products. In all the examples studied, a large excess of acid is necessary completely to effect the reaction, and this fact lends colour to the assumption that the salts which undergo the change are of the di-acid type (X). It is apparent that these



salts would be converted into the azothionium salts by the loss of the elements of water, the complete process being represented as follows:

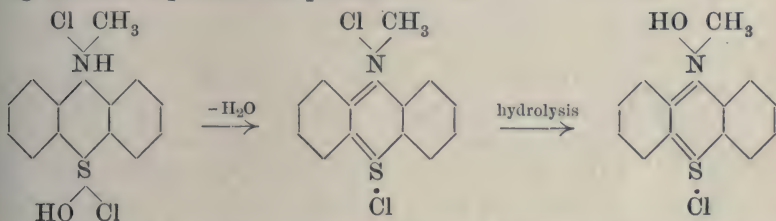


Moreover, it is apparent that whether the resulting quinonoid salt (XI) can be isolated or not must depend on the basic character of the sulphonium and ammonium groups, and this is controlled by the nature and number of the groups present in the aromatic

nuclei (Kehrmann, *Ber.*, 1906, **39**, 914; Smiles and Hilditch, *Trans.*, 1908, **93**, 1691). For example, the parent phenazothionium compound is obtained as the monohalide (XII) (*Trans.*, 1909, **95**, 1259), whilst the di- and tetra-nitro-derivatives, being completely hydrolysed during the process of isolation, appear as sulphonium hydrates (XIII).

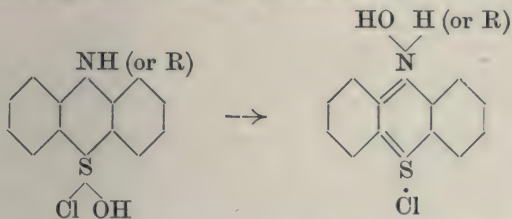
It is necessary to observe that this explanation of the process satisfactorily accounts for the invariable occurrence in the azothionium compounds of an additional molecule of water, which is so difficult to remove as to give rise to the suspicion that it is not merely water of crystallisation.

Moreover, a satisfactory account is given of the conversion of the *N*-methyl sulfoxide to the sulphonium compound. The following formulæ represent the process:



In this case it must remain doubtful whether hydrolysis takes place at the ammonium or sulphonium group, but the formula given for the product is the more probable of the two alternatives, for with the parent compound there can be no doubt that the product is the sulphonium halide, since it has been isolated in the anhydrous condition (Kehrmann, *Ber.*, 1901, **34**, 4170).

The alternative hypothesis of migration of hydroxyl from quadrivalent sulphur to tervalent nitrogen in the sulfoxide salt affords an equally satisfactory explanation of the change. From this point of view the reaction must be regarded as a true intramolecular rearrangement, being represented as follows:



But, as previously remarked, we are at present unable to offer any decisive evidence for the preference of either alternative hypothesis. On general grounds, the former of the alternatives given seems the more probable.

In conclusion, it must be stated that the hypothesis described is advanced to account for the following facts:

(1) The immobility of the alkyl group during the conversion of *N*-methyldiphenylamine *o*-sulphoxide.

(2) The more basic the character of the sulphoxide, the more readily does the change take place with a given acid reagent.

(3) The conversion of a given sulphoxide proceeds more easily the stronger the acid employed.

(4) The absorption of the elements of water during the reaction.

The results of the study of this reaction may be summed up as follows:

(1) The conversion of diphenylamine sulphoxides to phenazothionium derivatives does not take place by direct migration of hydrogen from the imino-group to the oxygen of the thionyl group.

(2) The salts of the imino-sulphoxides are first formed with the acid reagent, and these are then converted into the phenazothionium salt either (*a*) by loss of the elements of water, or (*b*) by migration of hydroxyl from the quadrivalent sulphur to tervalent nitrogen.

Preliminary experiments have shown that the conversion of the thionyl group to the quinonoid thionium arrangement may be effected not only in other cyclic systems, but also in hydroxy- and amino-sulphoxides. These substances are now being investigated.

In conclusion, we desire to thank the Research Fund Committee of the Chemical Society for a grant which has defrayed the expense of this research.

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XXI.—*The Adsorption of Uranium-X by Barium Sulphate.*

By ARTHUR JOHN BERRY, B.A.

BEQUEREL has shown (*Compt. rend.*, 1900, **131**, 137; 1901, **133**, 977) that when barium is precipitated as sulphate in a uranium solution, the photographic activity of the latter is removed by the barium sulphate. A similar result was obtained by Sir William Crookes (*Proc. Roy. Soc.*, 1900, **66**, 409), who found that uranium compounds could be obtained photographically inactive by a single chemical operation, the whole of the photographic activity being concentrated in a small residue termed uranium-X by Crookes. Soddy (*Trans.*, 1902, **81**, 860) showed that the whole of the β -ray

activity of uranium is due to the uranium- X , which is one of the disintegration products of uranium (Rutherford and Soddy, *Phil. Mag.*, 1903, [vi], 5, 441).

In the present communication, the adsorption of uranium- X has been investigated quantitatively, and evidence has been obtained of a definite "partition coefficient" between the uranium- X in the barium sulphate and in the solution. As the experiments were approaching completion, the author's attention was directed to a paper by Ritzel (*Zeitsch. physikal. Chem.*, 1909, 67, 724). Ritzel investigated the absorption of uranium- X by carbon, and he mentions (*loc. cit.*, p. 727): "Als Adsorbens wollte ich zunächst Bariumsulphat verwenden Vorversuche zeigten aber bald dass das Bariumsulphat, von Versuch zu Versuch, mit sehr schwankender Kristallgrosse ausfällt, und man kann deshalb keine guten Resultate erhalten." The present writer did not experience any difficulty of that kind. It was usually found perfectly easy to repeat a result under any given conditions. However, the use of barium sulphate is a disadvantage in studying the effect of time in the adsorption of uranium- X , as it is probable that the crystals would increase in size with lapse of time.

EXPERIMENTAL.

A solution of pure uranyl nitrate (Merck), containing 400 grams per litre, was employed. This solution was in radioactive equilibrium. Experiments were always carried out with 25 c.c. of this solution. The β -ray activity due to the uranium- X in this quantity of material was determined by Crookes's original method (*loc. cit.*). The liquid was diluted considerably, heated to boiling, a trace of ferric chloride added, and ammonium carbonate added in quantity sufficient to redissolve the precipitate of uranium carbonate. The liquid was then filtered from the ferric hydroxide, and the activity of the uranium- X , removed by the latter, measured by a β -ray electroscope.

This electroscope was of the ordinary single-leaf type. The case of the instrument was a stout brass cylinder, the internal diameter being 10.1 cm., and the internal height 12.6 cm. The base of the electroscope was of aluminium foil 0.1 mm. thick. The preparations were placed on a board at a fixed distance (7.7 cm.) below the base of the instrument. The rate of leak was determined in the usual way with a reading microscope and a stop-watch. In every case, the "natural leak" of the instrument was determined and allowed for. This natural leak varied but slightly, the usual value being 3.7 scale divisions per minute. The measurements were always compared with the leak due to a standard consisting of black

uranium oxide. The mean of three concordant determinations of the β -ray activity in 10 grams of uranyl nitrate carried out in this manner was 106.6 scale divisions per minute.

It was always possible to separate more than 90 per cent. of the uranium- X in the first operation by Crookes's method. On acidifying the filtrate with nitric acid, and repeating the process, practically all the remaining uranium- X was removed. This was checked by testing the residue after ignition.

Unless otherwise stated, the experiments were conducted as follows. The measured quantity of uranyl nitrate solution was taken, acidified with a given quantity of a 10 per cent. solution of sulphuric acid, and a quantity of water added, which, together with the quantity of standard barium nitrate (2.5 grams per litre) employed for precipitation, would make the solution up to some definite volume. The precipitation was carried out in the cold, and the liquid kept overnight. The solution was then boiled for one minute, the barium sulphate collected, and its β -ray activity measured. The absorption of the β -radiation in the barium sulphate may be neglected, since the greatest mass of precipitate on the filter paper was only 0.11 gram.

If there is a definite equilibrium between the uranium- X in the barium sulphate and in the liquid, we should have:

$$\frac{C_{\text{BaSO}_4}}{C_{\text{liquid}}^n} = k,$$

where C is the concentration of the uranium- X , and k and n are constants. The concentration in the barium sulphate is x/m , where x is the amount of uranium- X adsorbed, and m the mass of barium sulphate. The concentration in the liquid is $a - x/v$, where a is the initial quantity of uranium- X and v is the volume of the solution. If there is equilibrium we should have:

$$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n} = \text{constant}.$$

Series I.— $a=106.6$ divisions per minute. 1 c.c. of 10 per cent. sulphuric acid added to liquid. $v=150$ c.c.

m (gram).	x (divisions per minute).	$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n}$
0.0044	2.7	0.74
0.0088	5.3	0.72
0.0110	6.3	0.72
0.0154	8.1	0.73
0.033	14.7	0.74
0.044	19.3	0.74
0.066	21.8	0.77
0.088	24.1	0.78

Series II.— $a=106.6$ divisions per minute. 10 c.c. of 10 per cent. sulphuric acid added to liquid. $v=250$ c.c.

m (gram).	x (divisions per minute).	$\frac{\log(a-x)}{\log \frac{x}{m}} = \frac{1}{n}$.
0.0044	4.1	0.68
0.0110	15.1	0.63
0.022	38.7	0.57
0.033	47.7	0.56
0.044	54.7	0.56
0.055	60.3	0.55
0.088	70.3	0.54
0.110	76.9	0.52

Series III.—In this series the procedure was somewhat different. The uranium-*X* from one quantity (25 c.c.) of uranyl nitrate was removed by successive precipitations on separate days. The filtrates were always made up to a constant volume (140 c.c.), and precipitated each day by 10 c.c. of the solution of barium nitrate; 15 c.c. of 10 per cent. sulphuric acid were added at the beginning of the series only. $v=150$ c.c. In calculating $1/n$, a correction was made for the value of $(a-x)$, owing to the solution recovering its uranium-*X* content with time. The correction was made by a recovery curve for uranium-*X*. $m=0.022$ gram. a (initially) = 106.6 divisions per minute.

x (divisions per minute).	$(a-x)$ (corrected for recovery of Ur.- <i>X</i>).	$\frac{\log(a-x) \text{ (corrected)}}{\log \frac{x}{m}} = \frac{1}{n}$.
43.7	64.6	0.55
30.4	35.8	0.50
17.3	21.0	0.46
10.0	13.7	0.43
5.6	11.0	0.43

Series IV.—This series is precisely similar to series III, excepting that 20 c.c. of 10 per cent. sulphuric acid were added to start with. $v=150$ c.c., $m=0.022$ gram, and a (initially) = 106.6 divisions per minute.

x (divisions per minute).	$(a-x)$ (corrected for recovery of Ur.- <i>X</i>).	$\frac{\log(a-x) \text{ (corrected)}}{\log \frac{x}{m}} = \frac{1}{n}$.
45.0	63.0	0.54
30.4	34.7	0.49
17.0	20.1	0.45
8.7	13.9	0.44
5.6	11.2	0.44

From series I and II, it is evident that dilution and excess of sulphuric acid favour the adsorption of uranium-*X*, other things being equal. The influence of these two factors, separately, was confirmed by numerous other experiments, which it is unnecessary to describe here.

Series III and IV are of interest, inasmuch as continually diminishing the concentration of the uranium-*X* in the solution scarcely affects the constancy of $1/n$.

With regard to the effect of time, the following experimental facts may be of interest. It was found that as much uranium-*X* was adsorbed by the barium sulphate two hours after precipitation as when the liquid was kept all night after precipitation. But if the liquid was kept for three days before collecting the barium sulphate, the quantity of uranium-*X* adsorbed was greater. This would appear to indicate that adsorption takes place very rapidly at first, but that diffusion of the uranium-*X* into the barium sulphate particles takes place afterwards, and this latter process goes on for a considerable time. However, no great importance is to be attached to these time experiments, owing to the probable increase in size of the adsorbing particles. For the same reason, it is difficult to obtain evidence as to whether there is a definite equilibrium between the uranium-*X* in the solid and liquid phases which can be approached from both sides. Such a reversible equilibrium has been shown to exist in the case of the partition of uranium-*X* between carbon and solution by Ritzel (*loc. cit.*, p. 735); who finds that for this equilibrium the equation $C_l = \text{constant} \times C_k$, where C_l and C_k denote the concentration of the uranium-*X* in the solution and in the carbon respectively.

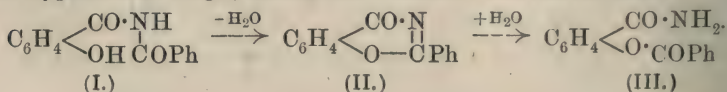
The author desires to express his sincere thanks to Mr. Soddy for the interest he has taken in these experiments and for his valuable suggestions.

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XXII.—2-Phenyl-1 : 3-benzoxazine-4-one.

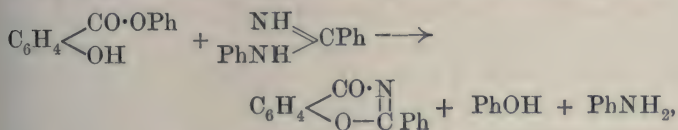
BY ARTHUR WALSH TITHERLEY.

In his criticism of the metoxazone theory of labile isomerism in the acylsalicylamide group, Auwers (*Ber.*, 1907, **40**, 3506) attributed the change of *N*-benzoylsalicylamide (I) to *O*-benzoylsalicylamide (III) (by boiling with acetic acid) to the intermediate formation of the unsaturated ring (II) by loss of water, which then immediately decomposed this hypothetical ring, yielding the *O*-benzoyl derivative, thus :



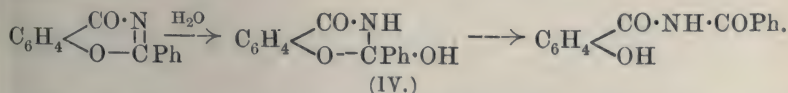
This view was shown to be untenable by Titherley and Hicks (Trans., 1909, 95, 908), but it appeared desirable to effect if possible the synthesis of this ring-compound in order that a study of its properties might be made in relation to the derivatives in the acyl-salicylamide group. Several attempts were made to prepare it from phenylbenzometoxazone, * $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \diagdown \quad | \\ \text{O} \quad \text{C} \text{HPh} \end{smallmatrix}$, by eliminating two hydrogen atoms, and from *O*- and *N*-benzoylsalicylamides by the action of dehydrating agents, like phosphoric oxide and zinc chloride, but without success.

Eventually the compound was synthesised from phenyl salicylate and phenylbenzamidine by loss of phenol and aniline, thus:



and it was later found that the same ring-compound could be obtained when special precautions were observed, by the action of hydrogen chloride on either *N*- or *O*-benzoylsalicylamide at temperatures between 110° and 140°. These independent syntheses, which are discussed later, and the properties of the compound place its constitution beyond doubt, and it is, therefore, 2-phenyl-1:3-benzoxazine-4-one.

The compound has the same melting point, 106°, as that of its isomeride, benzoylsalicylnitrile, $\text{CN} \cdot \text{C}_6\text{H}_4 \cdot \text{OBz}$, from which, however, it differs greatly. It is markedly additive in properties, and its most striking addition is with water. With pure water or dilute alkalis it is almost unaffected, but in presence of hydrogen ions it rapidly adds one molecule of water, a quantitative yield of *N*-benzoylsalicylamide being produced. This simple circumstance finally disposes of Auwers's hypothetical contention which involves direct hydrolytic rupture at the double linking, but is intelligible on the author's theory that the intermediate hydroxy-derivative (IV) is too unstable to exist, as already frequently indicated, and at once rearranges to *N*-benzoylsalicylamide, thus:

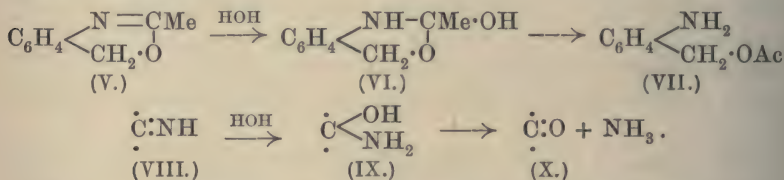


The still alternative explanation that hydrolytic rupture takes place

* The correct name of this compound is 2-phenyldihydro-1:3-benzoxazine-4-one but in view of its use in previous papers, "phenylbenzometoxazone" is retained in the present one.

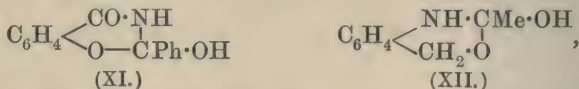
between the phenolic oxygen atom and the carbon atom to which the phenyl group is attached, is discounted by the comparatively great stability of the unsaturated ring-compound with alkali, which would favour such a rupture, and the only possible mechanism appears to be the above, which is identical with that occurring in the conversion of nitriles into amides through the agency of acids.

The above mechanism throws some light upon the decomposition by water in presence of hydrogen ions of certain allied compounds in which the double linked C:N pair appears in the molecule. Auwers observed (*Ber.*, 1904, 37, 2249) that the comparatively stable unsaturated ring (V) yields a hydrobromide which in aqueous solution adds water and passes into the salt of *o*-aminobenzyl acetate (VII), whilst J. F. Thorpe has shown that all true imino-compounds (VIII) are at once decomposed by dilute acids, giving ketonic derivatives (X). In these cases a similar mechanism is evidently at work, in which (1) the hydroxyl group attaches itself to carbon and the hydrogen atom to nitrogen, and (2) the resulting unstable compound (VI or IX) changes either by wandering of a hydrogen atom or by loss of ammonia into a stable derivative :



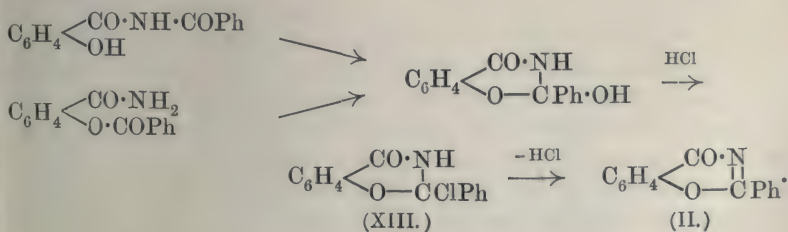
That such intermediate hydroxy-compounds are first formed in the cases observed by Auwers and Thorpe appears to follow from the complete analogy of these reactions to that of 2-phenyl-1:3-benzoxazine-4-one, where the production of the intermediate hydroxy-compound must be admitted on the grounds already stated and in view of the author's previous observations.

Contrasting the intermediate hydroxy-derivatives in the author's case (XI) with that of Auwers (XII) :



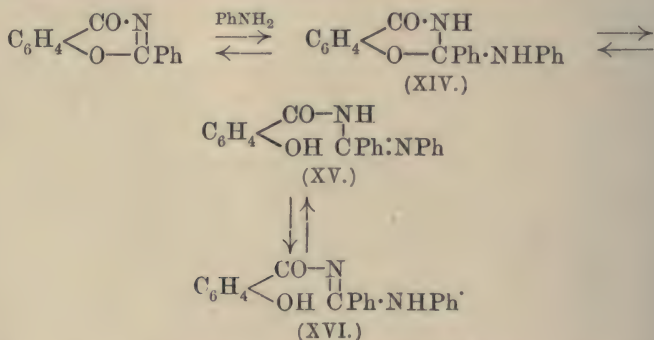
it is clear that when the hydrogen atom of the hydroxyl group wanders, (XI) yields an *N*-acyl derivative, whilst (XII) yields an *O*-acyl derivative. Theoretically, each could yield an *O*- or *N*-acyl derivative according to whether the hydrogen atom wandered to nitrogen or to the phenolic oxygen atom, and the final result probably depends on the conditions which favour one or other of these alternatives. Thus, in Auwers's case it is natural that the hydro-

bromic acid would favour the production of the *O*-acyl derivative, which is a base and yielded the salt, rather than the neutral *N*-acyl derivative, which is an amide. In the author's case neither the *O*- nor *N*-benzoylsalicylamide is a base, and the rearrangement yields simply the stable form (*N*-benzoyl). At the same time it must be noted that, although neither of the isomerides is a base in the ordinary sense, *O*-benzoylsalicylamide as a primary amide must be more basic than its isomeride, which is secondary. Experiments which have been made on the two isomerides show that the former is more basic, and yields a definite hydrochloride when treated in presence of benzene with hydrogen chloride. It might therefore be anticipated that hydrogen chloride should effect the rearrangement of *N*-benzoylsalicylamide into its isomeride [through the hydroxy-form (XI)]. Such a change has already been partly effected by continued boiling with pure acetic acid (McConnan and Titherley, Trans., 1906, 89, 1331), a fact which supports the supposition that the intermediate hydroxy-form may open in either of the two alternative ways according to conditions (acetic acid favouring the production of the more basic *O*-benzoyl derivative). Experiments on the action of hydrogen chloride on *N*-benzoylsalicylamide in benzene showed that no change took place in the cold, but that in presence of boiling xylene slow and incomplete rearrangement to *O*-benzoylsalicylamide occurred. As the experiments proceeded, however, it became apparent that, besides rearrangement, chemical elimination of water was taking place at about 130°. By using ethylene dibromide or anisole as solvents and distilling off the water as produced, the latter action was accelerated, and 2-phenyl-1:3-benzoxazine-4-one was formed in large quantities. The latter was even more easily obtained by the action of hydrogen chloride on *O*-benzoylsalicylamide in boiling toluene or xylene if the water formed was continually removed. The hydrogen chloride virtually behaves as a catalyst, since relatively small quantities were found to be sufficient to effect the change. It is probable that the loss of water is not due to direct dehydration, but to the intermediate formation of the chloro-derivative (XIII), which immediately loses hydrogen chloride and apparently is incapable of existence:



When 2-phenyl-1:3-benzoxazine-4-one (II) in benzene solution is treated with dry hydrogen chloride, a white, crystalline compound containing chlorine is precipitated, which on exposure to atmospheric moisture rapidly passes into *N*-benzoylsalicylamide, but on treatment with aniline yields a yellow, crystalline solid, melting at 106°, which was found to have the constitution $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CPh}\cdot\text{NHPh}$ (salicylphenylbenzamidine). From this behaviour it was supposed that the ring-compound had added hydrogen chloride, giving the chloro-compound (XIII), or, by rearrangement, the compound $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}\cdot\text{CClPh}$, either of which might be expected to behave as above with water and aniline (see below). But from the fact that the hydrogen chloride additive product in presence of benzene regenerates the original ring-compound (II) with alkali, and from its other properties, it must be concluded that the product is merely the

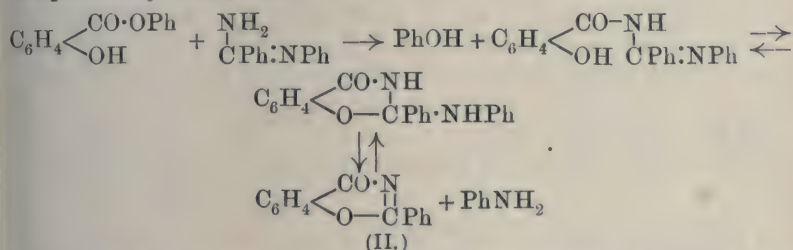
salt, $\text{C}_6\text{H}_4\left\langle \begin{array}{c} \text{CO}\cdot\text{N}\cdot\text{HCl} \\ | \\ \text{O}-\text{CPh} \end{array} \right.$, which with water would at once give *N*-benzoylsalicylamide (as explained above); whilst its curious behaviour with aniline subsequently became clear when it was found that the free ring-compound itself readily unites with aniline, producing the above amidine derivative according to the following scheme:



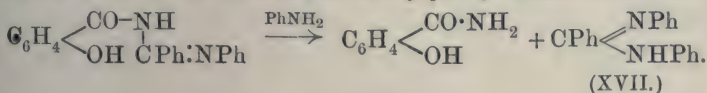
The reaction is reversible, and the anilino-derivative (salicylphenylbenzamidine) is a tautomeric substance. Its tautomerism comprises the three forms (XIV), (XV), and (XVI), of which the last two represent ordinary amidine tautomerism, and it is evident that one of these two formulæ must be given to the substance itself, melting at 106°, because of its phenolic properties. It loses aniline, however, below 100°, and passes quantitatively into 2-phenyl-1:3-benzoxazine-4-one, provided that the aniline is removed, and the easy reversibility of the above process would seem to imply that the compound is bordering on the verge of ring-formation (XIV). That the phenolic hydroxyl group and the group $\cdot\text{CPh}\cdot\text{NPh}$ are in intimate steric association is confirmed by the difficulty with which the substance

dissolves in dilute aqueous sodium hydroxide, and at first it was supposed that the ring formula (XIV) must be adopted for the substance. This view, however, is inconsistent with the bright yellow colour of the substance, for whilst phenylbenzometoxazone and 2-phenyl-1:3-benzoxazine-4-one are colourless, the alkali and ammonia derivatives of *N*-acylsalicylamides are bright yellow, and the phenolic nature of the anilino-derivative is confirmed by the strong ferric chloride reaction it gives.

In the synthesis of 2-phenyl-1:3-benzoxazine-4-one by heating phenyl salicylate with phenylbenzamidine, this anilino-compound is the first product of the reaction, and it is owing to its reversible decomposition, as above, that the unsaturated ring compound (II) is obtained, and for the same reason the yield of the latter is comparatively small, thus:



A considerable quantity of diphenylbenzamidine (XVII) is also produced as a result of a secondary reaction, which also appears to be reversible, between the aniline and salicylphenylbenzamidine, thus:



EXPERIMENTAL.

2-Phenyl-1:3-benzoxazine-4-one.

(a) *Preparation from Phenyl Salicylate*:—(a) 21.4 Grams of phenyl salicylate and 19.6 grams of phenylbenzamidine were heated at 110° for six and a-half hours, during which aniline and phenol were produced in quantity. On cooling, the resulting viscid, yellow syrup was stirred with 150 c.c. of water and 100 c.c. of 10 per cent. sodium hydroxide to remove phenol and salicylphenylbenzamidine, and the yellow alkaline solution was decanted off. The remaining syrup was washed with water, dissolved in 200 c.c. of pure benzene, and the benzene solution washed with alkali and water. In order to remove aniline and diphenylbenzamidine, the benzene solution was shaken for a few minutes with about 300 c.c. of 5 per cent. sulphuric acid, the upper benzene solution washed with water, and then as rapidly as possible

shaken with dilute alkali, to remove the *N*-benzoylsalicylamide formed during washing with acid and to neutralise the remaining traces of acid. (During the former operation some loss was entailed, because of the great instability of the ring compound* in presence of dilute acid.)

The alkali extract was found to contain besides phenol, a considerable quantity of salicylphenylbenzamidine, which was precipitated on adding acid and then decomposed, giving *N*-benzoylsalicylamide. The acid extract contained aniline and diphenylbenzamidine. The latter was isolated (4 grams), and found to be identical with Wallach's compound (*Annalen*, 1877, **184**, 83).

The clear benzene solution was washed twice with water, dried, and evaporated at about 40°. Massive crystals remained, together with a syrupy portion, which crystallised after several hours. After washing with a little ether and draining on porous porcelain, the crude product (12.5 grams) was crystallised from 700 c.c. of light petroleum, the solution being allowed to cool very slowly to avoid deposition of syrup. White or transparent, colourless leaflets or plates (m. p. 104°; 10.5 grams) separated, which on recrystallisation from light petroleum were obtained in the pure state and then melted sharply at 106—107°:

0.2193 gave 0.6024 CO₂ and 0.0759 H₂O. C=74.92; H=3.85.

0.1688 „ 9.3 c.c. N₂ (moist) at 20° and 757 mm. N=6.28.

0.3480, by Kjeldahl's method, required 16.0 c.c. *N*/10-HCl. N=6.39.

C₁₄H₉O₂N requires C=75.34; H=4.03; N=6.27 per cent.

2-Phenyl-1:3-benzoxazine-4-one is very soluble in chloroform or acetone, readily so in benzene, methyl alcohol, or ethyl acetate, and rather less so in ethyl alcohol, ether, or pyridine. It dissolves in about 70 parts of light petroleum (b. p. 90—120°). It may be recovered unchanged after solution in these solvents, even pyridine. Its solutions give no coloration with alcoholic ferric chloride. In glacial acetic acid it readily dissolves, but owing to the presence of moisture the solution soon deposits *N*-benzoylsalicylamide.

Behaviour with Water.—The compound is insoluble in water, but on boiling an oil is produced which dissolves appreciably. The clear hot aqueous solution if rapidly cooled becomes turbid, and after a short time fine needles of the unaltered compound separate, but not without production of some *N*-benzoylsalicylamide. Its behaviour with water was studied by diluting an alcoholic solution largely, but insufficiently, to induce separation. The clear solution remained clear for about three hours, after which it became faintly turbid, owing to separation

* If ether is used instead of benzene as a solvent, the whole of the ring-compound is decomposed during the washing with acid.

of the highly insoluble *N*-benzoylsalicylamide, which, however, was not completely precipitated in twenty-four hours. Whether pure water free from carbonic acid would behave like ordinary distilled water has not been tried. Traces of acids (inorganic and organic) enormously accelerate the action of the water, and it was shown roughly that the velocity depends on the concentration of the acid added. If 20 c.c. of a 0.05 per cent. solution are treated with 0.05 c.c. of 10 per cent. hydrochloric acid, the decomposition is complete in about seventy seconds. Accurate velocity measurements have not been made, but the quantitative nature of the conversion was easily shown by decomposing a known weight in dilute alcohol. On acidifying the clear solution with a few drops of hydrochloric acid, after a few seconds a voluminous, microcrystalline precipitate* separated, which was collected and dried at 100°:

0.2230 gave 0.2398 *N*-benzoylsalicylamide.

$C_{14}H_9O_2N$ requires 0.2410 *N*-benzoylsalicylamide.

The purity of the *N*-benzoylsalicylamide was shown by the sharp melting point (206°) before recrystallising.

Behaviour with Acids.—The cyclic compound has only a weakly basic character, and with aqueous acids is decomposed without previously dissolving. It does not yield a picrate in benzene or alcoholic solution. Dry hydrogen chloride in benzene solution precipitates its hydrochloride, which, however, could not be isolated in a pure condition for analysis, owing to the great ease with which it is decomposed by atmospheric moisture.

Behaviour with Alkalis.—With cold aqueous sodium hydroxide and ammonia, the compound is comparatively stable and only very slowly changed to the salt of *N*-benzoylsalicylamide, but sodium hydroxide immediately decomposes it in alcoholic solution. Dry ammonia produces a yellow colour with an alcoholic solution of the compound, and probably an additive compound like that obtained with aniline is formed; this is under investigation.

Behaviour with Phosphorus Pentachloride—The compound, on treatment with phosphorus pentachloride in presence of chloroform, instantly gives a bright lemon-yellow, crystalline solid,



identical with that obtained by Titherley and Hicks (*loc. cit.*) by the action of phosphorus pentachloride on phenylbenzometoxazone at higher temperatures.

Reduction.—The reduction of 2-phenyl-1:3-benzoxazine-4-one

* The reaction affords a very delicate test for 2-phenyl-1:3-benzoxazine-4-one. On dissolving a minute amount in a drop of alcohol and treating with about 1 c.c. of water and a trace of any dilute acid, a precipitate appears suddenly after a few seconds.

cannot be effected by sodium amalgam, in alkaline solution, or by acid reducing agents, owing to ring rupture. With aluminium amalgam, however, the reduction proceeds rapidly.

A dilute alcoholic solution of the substance was treated with an excess of aluminium amalgam, and water added gradually. When the reduction was complete, the alcoholic solution was filtered and allowed to evaporate. The resulting solid was washed with dilute alkali, dried, and extracted with boiling alcohol. A white, sparingly soluble solid remained behind, which has not yet been identified, and the alcoholic solution deposited needles consisting of impure phenylbenzometoxazone. By carefully recrystallising from alcohol, the latter was obtained pure in fine needles melting at 169° , and was easily identified. The melting point after mixing with a specimen of phenylbenzometoxazone synthesised from salicylamide and benzaldehyde was $168-169^{\circ}$. The yield was about 30 per cent., and a similar reduction performed in an ethereal solution containing 5 per cent. of alcohol gave a yield of 40 per cent.

(b) *Preparation from O-Benzoylsalicylamide.*—A mixture of 3 grams of *O*-benzoylsalicylamide and 30 c.c. of xylene contained in a distilling flask was heated in a bath to 145° , and when the solution became clear a stream of dry hydrogen chloride was passed in for a few minutes. By gradually raising the temperature of the bath to 155° , the xylene was allowed to distil over drop by drop, carrying with it the water formed in the reaction. The hydrogen chloride acted catalytically, and only a relatively small quantity was necessary, but in order to make good that lost by distillation, a few bubbles of the gas were passed into the liquid at intervals of three minutes. The rate of distillation was regulated so that the majority of the xylene had passed over in an hour. About 0.2 gram of water passed over with it, and an oil remained in the flask which partly crystallised on cooling and consisted of a mixture of 2-phenyl-1:3-benzoxazine-4-one and its hydrochloride and unchanged *O*-benzoylsalicylamide, together with a little xylene. When cold it was treated with 20 c.c. of benzene and well shaken with an excess of 3 per cent. sodium hydroxide. A considerable quantity of lemon-yellow solid (the sodium derivative of *N*-benzoylsalicylamide produced by rearrangement of *O*-benzoylsalicylamide) separated, which was mostly removed by repeatedly washing the benzene extract with water. The benzene extract was then dried, filtered, and evaporated at 50° , when large, colourless plates were left, together with an oil which crystallised on cooling. The solid was practically pure 2-phenyl-1:3-benzoxazine-4-one, and weighed 1.8 grams, or 65 per cent. of the theoretical yield. On recrystallising from about 100 c.c. of light petroleum and cooling slowly,

it separated in small, colourless, glistening plates, which melted sharply at 106° , and a mixture with a specimen obtained by the amidine method of synthesis also melted at 106° :

0.2128 gave 0.6003 CO_2 and 0.0755 H_2O . $\text{C} = 76.8$; $\text{H} = 3.9$.

0.1812 „ 0.5070 CO_2 „ 0.0635 H_2O . $\text{C} = 76.32$; $\text{H} = 3.89$.

0.2362 „ 13.7 c.c. N_2 (moist) at 23° and 755 mm. $\text{N} = 6.49$.

$\text{C}_{14}\text{H}_9\text{O}_2\text{N}$ requires $\text{C} = 75.34$; $\text{H} = 4.03$; $\text{N} = 6.27$ per cent.

The properties of the substance agreed in every particular with those of the compound obtained by the amidine method.

In a similar preparation to the above, using toluene instead of xylene as solvent, the compound was also obtained, but the yield was lower (36 per cent. of the theoretical).

(c) *Preparation from N-Benzoylsalicylamide*.—A similar method to the above was employed, using anisole as a solvent at 130° . About two and a-half hours were required for the completion of the change, and a yield of 60 per cent. of 2-phenyl-1:3-benzoxazine-4-one (m. p. 106 — 107°) was obtained. Ethylene dibromide was also used with success as a solvent, but xylene was unsatisfactory, owing to the small solubility of *N*-benzoylsalicylamide. During the action of the hydrogen chloride, some of the *N*-benzoylsalicylamide is rearranged to *O*-benzoylsalicylamide, and this was isolated in small quantity in one experiment, when xylene was used as solvent, as needles melting with rearrangement at 144° .

Salicylphenylbenzamidine,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{N}:\text{CPh}\cdot\text{NH}$ $\text{P} \rightleftharpoons \text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NPh}$,
was obtained by the action of aniline on 2-phenyl-1:3-benzoxazine-4-one or its hydrochloride by the following methods.

One gram of 2-phenyl-1:3-benzoxazine-4-one and 0.5 gram of aniline were warmed to 50° , and the resulting yellow oil, which did not crystallise on cooling, was dissolved in 50 c.c. of boiling light petroleum and the clear yellow solution allowed to cool slowly. A yellow syrup was deposited, which, after being kept for twelve hours in contact with the mother liquor, changed to a mass of beautiful transparent, yellow needles (1.3 grams), and the mother liquor yielded a further quantity (0.1 gram), the total yield being 93 per cent. of the theoretical.

When instead of light petroleum as a solvent, ether (15 c.c.) was used, the pure compound separated after several hours in clusters of needles (0.9 gram) without any syrup being first deposited, and a further quantity (0.2 gram) was obtained from the mother liquor. The substance was also prepared in the pure state by treating a benzene suspension of 2-phenyl-1:3-benzoxazine-4-one hydrochloride with aniline. The identity of the yellow needles obtained by the

different methods was shown by a comparison of melting point (105—107°) and other properties:

0.2750 gave 19.8 c.c. N_2 (moist) at 17° and 772 mm. $N = 8.50$.

$C_{20}H_{16}O_2N_2$ requires $N = 8.86$ per cent.

Salicylphenylbenzamidine is somewhat sparingly soluble in ether, moderately so in alcohol, and readily soluble in chloroform or benzene. Its solutions give a reddish colour with alcoholic or ethereal ferric chloride. Its solutions on evaporation at the laboratory temperature yield syrups which crystallise completely only after several days, and it is probable that two or more isomeric forms in equilibrium are produced by labile change when the yellow needles are dissolved in any solvent. If heated in a light petroleum solution for any length of time, as in crystallising large quantities, the substance more or less dissociates into aniline and 2-phenyl-1:3-benzoxazine-4-one, which separates to some extent on cooling in colourless needles or tufts alongside the yellow needles of the unchanged substance. Prolonged boiling leads to decomposition of a portion, owing to the action of the aniline (see below) forming diphenylbenzamidine.

Salicylphenylbenzamidine possesses weakly basic and weakly phenolic characters; it is soluble in, but at once decomposed by, hydrochloric acid, yielding *N*-benzoylsalicylamide. In a condition of fine powder it is only very slowly soluble in dilute sodium hydroxide; a yellow solution of the sodium salt results, from which, however, it is apparently impossible to recover the original substance; on acidification with hydrochloric acid, a yellow precipitate is formed, soluble in excess of acid to a nearly clear solution, from which *N*-benzoylsalicylamide is almost instantly precipitated. When salicylphenylbenzamidine is heated at 95°, it dissociates, and eventually melts to a clear yellow liquid with an odour of aniline; if the latter is allowed to evaporate slowly in an open shallow vessel, the yellow colour becomes less conspicuous, and at the end of some hours a colourless liquid results, which finally sets to a mass of colourless plates, consisting of 2-phenyl-1:3-benzoxazine-4-one, the yield of which was almost theoretical. When heated with aniline at 100° for several hours, salicylphenylbenzamidine is partly decomposed into salicylamide and diphenylbenzamidine, the latter obtained in a yield of 35 per cent.

XXIII.—*Iodobenzenemonosulphonic Acids. Part II.
Esters and Salts of Di- and Tri-iodobenzenesulphonic
Acids.*

By MARY BOYLE.

IN the first communication on this subject (Trans., 1909, **95**, 1683) a brief account was given of the preparation of 2: 5- and 3: 4-di-iodo-benzenesulphonic ethyl esters. It was stated that they were obtained when the sulphonyl chloride was treated either with alcohol in the presence of sodium hydroxide or, when dissolved in ether, with a solution of sodium ethoxide in alcohol, but beyond the further statement that they melted at 113° and 81° respectively, no account of their properties was submitted, and no analytical results were given. Further experiments on ester formation have made clear that neither of the above methods is satisfactory as regards yield and purity of the product unless careful attention is paid to the proportions of interacting substances and to the duration of the action, and the ester melting at 113° , prepared without such attention to detail, proved, on analysis, to be slightly contaminated with the sulphonyl chloride from which it was formed, the pure ester melting about 6° higher. Under the right conditions, however, it has been found possible to esterify all the iodo-benzenesulphonic acids discussed in Part I., and to obtain very well-characterised methyl and ethyl derivatives.

Methyl and ethyl benzenesulphonates were prepared by Hübner (*Annalen*, 1884, **223**, 237) by the action of sodium alkyl oxides free from alcohol on solutions of the sulphonyl chlorides in absolute ether, and by Krafft and Roos (*Ber.*, 1892, **25**, 2257) by allowing the chloride to remain for many days at low temperatures in contact with pure methyl and ethyl alcohols respectively; *p*-chloro- and *p*-bromo-benzenesulphonic and certain naphthalenesulphonic methyl and ethyl esters were described by the same experimenters, and the corresponding *p*-iodo-derivative was prepared in 1895 by Kastle and Murrill by the use of sodium ethoxide (*Amer. Chem. J.*, **17**, 290).

In Krafft's experiment with chloride and alcohol alone, the employment of low temperatures seemed imperative, since, as was stated in a later communication (*Ber.*, 1893, **26**, 2823), complete hydrolysis occurred when the two were heated together in sealed tubes, or, in a few cases, when heated for a short time on the water-bath. On the other hand, there is the statement by H. E. Armstrong (*Proc.*, 1891, **7**, 184) that many dibromo-

naphthalenesulphonyl chlorides are readily converted into esters by boiling with excess of alcohol, the 1:4-dibromo-compound being especially remarkable for the ease with which it is esterified, a very small proportion only undergoing hydrolysis; some isomeric sulphonyl chlorides, however, are, according to him, hydrolysed almost completely under exactly the same conditions.

In preparing di- and tri-iodo-benzenesulphonic esters, both methods have been made use of, and it is interesting to note that isomeric acids often behave very differently under similar experimental conditions, the orientation of the molecule appearing to influence to some extent the stability both of the sulphonyl chloride and of the alkylated sulphonic group. The insolubility of most of the sulphonyl chlorides in cold alcohol rendered the success of Krafft's method improbable, and the one experiment which was made proved quite unsuccessful; all of them, however, dissolved in hot alcohol with more or less ease, with gradual esterification.

The tri-iodo- dissolved with much more difficulty than the di-iodo-compounds, and the crystals which separated from the cooled clear solution were much less contaminated with unchanged chloride than was the case when di-iodo-compounds were under investigation. Of the three tri-iodobenzenesulphonyl chlorides investigated, the 3:4:5-derivative dissolved in boiling absolute alcohol with most difficulty and yielded the purest product, the 2:3:5-derivative dissolved with least difficulty, but yielded a product which only became homogeneous after repeated re-solution; the 2:4:5-derivative seemed to lie intermediate between these two.

It seems probable, then, that it is the contiguity of the iodine atom to the sulphonyl chloride group that renders the latter difficult of attack by the alcohol; in every case, however, a hydrolysing action accompanies esterification, the yield of ester under the most favourable conditions never realising more than 60 to 70 per cent.

In the case of the di-iodosulphonyl chlorides, no quantitative experiments have been carried out, but none seem necessary in view of their very decided differences in behaviour towards alcohol.

There is no doubt that the symmetrical 3:5-derivative yields an ester which is practically pure after one recrystallisation, that the 2:5- and 3:4-derivatives are attacked with about equal difficulty, and that the 2:4-derivative cannot be made to yield an ester at all by this method, so that here again, with the doubtful exception of the 2:5-derivative, inhibition seems to be a question of the contiguity of the iodine atom and sulphonic group.

The exceptional behaviour of 2:5-di-iodobenzenesulphonyl chloride towards alcohol is in accord with Armstrong's statement with respect to the behaviour of 1:4-dibromonaphthalenesulphonyl

chloride in the same circumstances (*loc. cit.*), and is also at one with the peculiar behaviour of the corresponding 2:5-ester towards alcohol, this ester being more easily hydrolysed by hot alcohol than any of the other ethyl di-derivatives, hydrolysis occurring to the extent of about 39 to 40 per cent. when the two substances are boiled together for five minutes.

The extent to which hydrolysis occurs when iodobenzenesulphonic esters are treated with hot alcohol was investigated in the first instance in order to ascertain the effect of the introduction of a second iodine atom on the stability of the ester. Kastle and Murrill have investigated the behaviour of benzenesulphonic ester and its *p*-chloro-, *p*-bromo-, and *p*-iodo-derivatives towards alcohol both at the ordinary temperature and at 100° (*Amer. Chem. J.*, 1895, 17, 292), and their results show clearly (1) that hydrolysis occurs very slowly at the ordinary temperature, not more than 19 per cent. being attacked in thirty days under the most favourable conditions (one part of ester to 50—100 parts of alcohol), (2) that hydrolysis takes place much more rapidly at 100°, about 9 per cent. undergoing change in five minutes, other conditions being the same, and (3) that the introduction of a halogen atom into the nucleus considerably weakens the stability of the ester, 20 to 21 per cent. now being changed in the same time as before; the three halogens seem to exert practically the same influence.

The introduction of a second and of a third iodine atom into the nucleus would be expected, therefore, still further to diminish the stability of the ester towards alcohol, and experimental results entirely confirm such a view, the average hydrolysis for di-iodo- and tri-iodo-benzenesulphonic esters being, after five minutes at 100°, about 30 to 33 per cent. The experiments, unlike Kastle's, were conducted under atmospheric pressure, equivalent weights of the different esters mixed with the same volume (about fifty times the theoretical amount) of absolute alcohol being heated under reflux in boiling water for five minutes; the cooled mixture was then either diluted with alcohol and titrated with *N*/10-sodium hydroxide, or the unchanged ester was precipitated with water, collected, and the filtrate and washings titrated as before. The latter method is perhaps the better, since the unchanged ester present during titration is slowly hydrolysed by the added sodium hydroxide; on the other hand, this hydrolysing action takes place so slowly that it is comparatively easy to detect the end-point of the acid-neutralisation.

In these experiments it is difficult to compare the tri-iodo- with the di-iodo-esters, and also the tri-iodo-esters among themselves, since two of these, namely, 3:4:5-tri-iodo- and 2:4:5-tri-iodo-

benzenesulphonyl ethyl esters, are so sparingly soluble in alcohol, even after careful powdering, that at the end of the five minutes' heating only a small proportion has passed into solution to be subjected to the hydrolysing action of the alcohol; the 2:3:5-ester, however, is as soluble as the di-iodo-compounds, so that results in the latter cases are strictly comparable. Such results show clearly that the greater the number of iodine atoms in the nucleus, the less the stability of the ethylated sulphonic group, ethyl monoiodobenzenesulphonate, according to Kastle, being hydrolysed to the extent of about 20 per cent. when heated to 100° with alcohol for five minutes, ethyl di-iodobenzenesulphonates, according to the author, undergoing from 25 to 35 per cent. hydrolysis, and ethyl 2:3:5-tri-iodobenzenesulphonate from 45 to 55 per cent.

The results obtained on directly titrating the hydrolysed solution of the ester are always slightly lower than the corresponding ones obtained after precipitation of the unchanged ester, a fact no doubt due to the hydrolysing action of water, which, although very slight and practically negligible at the ordinary temperature for a short period of time, may become of some account after the twelve hours necessary for complete precipitation.

From the experiments on the relative ease of hydrolysis of the four ethyl di-iodobenzenesulphonates, no absolutely definite conclusions can be drawn. All experiments seem to show that the 2:5-ester is the most easily hydrolysed by boiling absolute alcohol, and that the 3:5-ester comes next in order; most experiments place the 2:4-ester next in order of stability, and the 3:4-ester as the most stable of all and least easily affected; some experiments, however, interchange the order of the two latter substances. The following table shows the percentage hydrolysis which occurred in six different experiments:

Ester.	Percentage hydrolysis.					
	(1).	(2).	(3).	(4).	(5).	(6).
2:5-	39	39	—	27	32	—
3:5-	35	36	—	26	—	—
3:4-	24	24	24	24	22	27
2:4-	22	29	29	15	29	30
2:3:5-	57	—	54	50	—	—

The tri-iodo-ester is added for purposes of comparison.

In order to confirm Kastle's statement that the methyl esters are more easily attacked than are the ethyl derivatives by the corresponding alcohols, the action of methyl alcohol on methyl 2:5-di-iodobenzenesulphonate was investigated. Equivalent weights of the ethyl and methyl esters were boiled for five minutes with 10 c.c. of ethyl and methyl alcohol respectively, the unchanged

esters precipitated, and the filtrates titrated with *N*/10-sodium hydroxide.

The following results were obtained:

Ester.	Percentage hydrolysis.
2 : 5-ethyl ester	39·5
2 : 5-methyl ester	48

in complete accordance with Kastle's statement.

Since Krafft's method of preparing sulphonic esters had proved unsuccessful, and the method of boiling the sulphonyl chloride with alcohol unsatisfactory, since, also, the method consisting in treating the chloride with warm alcohol in presence of excess of sodium hydroxide resulted, in some cases, in almost complete hydrolysis, and, in all others, in very small yields of ester, the use of sodium alkyloxides was adopted.

In this case, again, poor yields were obtained, until it was recognised that a slight excess of the sodium alkyloxides was sufficient to cause precipitation of sodium iodobenzenesulphonates. By using a standard solution of sodium alkyloxide in absolute alcohol (about 2·5-*N*), by adding the slightest excess over the amount necessary to precipitate the chlorine from the sulphonyl chloride, and by keeping the mixture for about half a minute only before addition of water and separation of the ethereal layer, an almost quantitative yield of the ester was obtained. Under these conditions it was found unnecessary to use absolute ether as solvent; methylated ether (dehydrated) dried for some weeks with calcium chloride, and finally with sodium, was found pure enough for practical purposes.

The methyl esters were prepared in exactly the same way, and afforded no difficulty in purification.

Both ethyl and methyl esters crystallise extremely well from alcohol, from ether, and from a mixture of alcohol and ether. In the case of ethyl 2 : 3 : 5-tri-iodobenzenesulphonate, two very distinct sets of crystals were obtained from a mixture of alcohol and ether; they melt at the same temperature, and give identical analyses; moreover, one form is transformed into the other on recrystallisation from alcohol; they are evidently the same substance.

Salts of 3 : 4 : 5-, 2 : 4 : 5-, 2 : 3 : 5-tri-iodo-, and of 3 : 5- and 2 : 4-di-iodobenzenesulphonic acids, which were not described in Part I, have now been investigated; they are described in the experimental part of this paper.

The following table shows the melting points of the chlorides

and ethyl and methyl esters of di- and tri-iodobenzenesulphonic acids:

Acid.	Chloride.	Ethyl ester.	Methyl ester.
2:5-acid	132°	120·5°	106°
3:5-	93	112	95
3:4-	82	82	93
2:4-	77	57	78
2:3:4-	122·5	110	137
2:4:5-	135	156	166
3:4:5-	145	143	157

EXPERIMENTAL.

2:4-Di-iodobenzenesulphonic Acid.

The *ethyl* ester was prepared by dissolving the sulphonyl chloride in dry ether and adding the requisite amount of a solution of sodium ethoxide in absolute alcohol; after half a minute, water was added, and the ethereal layer separated and evaporated; the ester separated from alcohol in long needles, melting at 57°:

0·1489 gave 0·1199 CO₂ and 0·0246 H₂O. C=21·99; H=1·83.

C₈H₆O₃I₂S requires C=21·92; H=1·82 per cent.

The *methyl* ester was prepared from the sulphonyl chloride by the use of sodium methoxide in pure methyl alcohol. It crystallises from alcohol in large, plate-like needles, melting at 98°

0·1895 gave 0·1378 CO₂ and 0·0246 H₂O. C=19·84; H=1·44.

C₇H₆O₃I₂S requires C=19·81; H=1·41 per cent.

The *sodium* salt separates from water in white, glistening scales, containing two molecules of water of crystallisation:

0·2019 gave 0·1138 CO₂ and 0·0263 H₂O. C=15·37; H=1·44.

0·9138 lost 0·0702 at 150°. H₂O=7·68.

C₆H₃O₃I₂SNa, 2H₂O requires C=15·38; H=1·49;

H₂O=7·68 per cent.

Solubility.—One hundred grams of water dissolve 1·90 grams of anhydrous salt at 13°.

The *potassium* salt crystallises with one molecule of water in sparkling, plate-like needles:

0·2033 gave 0·1151 CO₂ and 0·0199 H₂O. C=15·52; H=1·09.

0·2059 „ 0·0383 K₂SO₄. K=8·35.

0·9375 lost 0·0407 at 145°. H₂O=4·34.

C₆H₃O₃I₂SK, H₂O requires C=15·45; H=1·07; K=8·37;

H₂O=3·86 per cent.

Solubility.—One hundred grams of water dissolve 0·76 gram of the anhydrous salt at 11·5°.

The *ammonium* salt crystallises in glistening, plate-like needles, which are anhydrous.

Solubility.—One hundred grams of water dissolve 2.23 grams at 14°.

3: 5-Di-iodobenzenesulphonic Acid.

The *ethyl* ester crystallises from ether or from a mixture of alcohol and ether in small, white needles, melting at 112°:

0.0591 gave 0.0406 CO₂ and 0.0103 H₂O. C=21.96; H=1.92.

C₈H₈O₃I₂S requires C=21.92; H=1.83 per cent.

The *methyl* ester separates slowly from alcohol in interlacing, plate-like needles, melting at 95°:

0.1159 gave 0.0840 CO₂ and 0.0155 H₂O. C=19.84; H=1.48.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

The *sodium* salt crystallises in white needles, containing one molecule of water of crystallisation:

0.1286 gave 0.0769 CO₂ and 0.0131 H₂O. C=16.30; H=1.12.

0.4892 lost 0.0195 at 140°. H₂O=3.99.

C₆H₃O₃I₂SNa, H₂O requires C=16.00; H=1.11;

H₂O=4.00 per cent.

Solubility.—One hundred grams of water dissolve 3.56 grams of anhydrous salt at 20°.

The *potassium* salt crystallises in large, white plates; the crystals are anhydrous:

0.1710 gave 0.1014 CO₂ and 0.0112 H₂O. C=16.16; H=0.66.

C₆H₃O₃I₂SK requires C=16.07; H=0.67 per cent.

Solubility.—One hundred grams of water dissolve 0.75 gram of salt at 18.5°.

The *ammonium* salt crystallises in fine, colourless, anhydrous needles.

Solubility.—One hundred grams of water dissolve 1.62 grams of salt at 20°.

The *barium* salt crystallises in colourless needles, containing 3½ molecules of water:

0.6225 lost 0.0380 at 145°. H₂O=6.10.

C₁₂H₆O₆I₄S₂Ba, 3½H₂O requires H₂O=6.18 per cent.

3: 4: 5-Tri-iodobenzenesulphonic Acid.

Ethyl 3: 4: 5-tri-iodobenzenesulphonate is obtained in a 55 per cent. yield by boiling the sulphonyl chloride with alcohol, in 90 per cent. yield by the use of sodium ethoxide. It separates from alcohol in long, transparent needles, melting at 143°:

0.1865 gave 0.1167 CO₂ and 0.0200 H₂O. C=17.09; H=1.20.

C₈H₇O₃I₃S requires C=17.02; H=1.24 per cent.

Methyl 3: 4: 5-tri-iodobenzenesulphonate crystallises from alcohol in needles, melting at 157° :

0.1461 gave 0.0811 CO_2 and 0.0130 H_2O . $\text{C}=15.15$; $\text{H}=0.98$.

$\text{C}_7\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.90$ per cent.

The *sodium* salt crystallises in small, white, sparkling needles, containing one molecule of water:

0.2642 gave 0.1213 CO_2 and 0.172 H_2O . $\text{C}=12.52$; $\text{H}=0.71$.

1.3331 lost 0.0421 at 150° . $\text{H}_2\text{O}=3.15$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}, \text{H}_2\text{O}$ requires $\text{C}=12.50$; $\text{H}=0.69$;

$\text{H}_2\text{O}=3.12$ per cent.

Solubility.—One hundred grams of water dissolve 0.86 gram of the anhydrous salt at 15° .

The *potassium* salt separates from water in white, anhydrous needles:

0.2027 gave 0.0944 CO_2 and 0.0073 H_2O . $\text{C}=12.69$; $\text{H}=0.39$.

0.2073 „ 0.0305 K_2SO_4 . $\text{K}=6.59$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}$ requires $\text{C}=12.54$; $\text{H}=0.34$; $\text{K}=6.79$ per cent.

Solubility.—One hundred grams of water dissolve 0.128 gram of salt at 16.5° .

The *ammonium* salt crystallises in long, anhydrous needles.

Solubility.—One hundred grams of water dissolve 0.25 gram of salt at 15° .

2: 4: 5-Tri-iodobenzenesulphonic Acid.

Ethyl 2: 4: 5-tri-iodobenzenesulphonate separates from alcohol in glistening crystals, which redissolve with difficulty in alcohol and ether. They melt at $155\text{--}156^{\circ}$:

0.1197 gave 0.1117 CO_2 and 0.0188 H_2O . $\text{C}=16.99$; $\text{H}=1.17$.

$\text{C}_8\text{H}_7\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=17.02$; $\text{H}=1.24$ per cent.

Methyl 2: 4: 5-tri-iodobenzenesulphonate separates in small, glistening crystals from a mixture of alcohol and ether. It melts at 166° :

0.1176 gave 0.0656 CO_2 and 0.0089 H_2O . $\text{C}=15.22$; $\text{H}=0.84$.

$\text{C}_7\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.90$ per cent.

The *sodium* salt crystallises in long, fine needles, slightly cream-coloured; they contain $1\frac{1}{2}$ molecules of water:

0.1532 gave 0.0699 CO_2 and 0.0114 H_2O . $\text{C}=12.44$; $\text{H}=0.82$.

0.4245 lost 0.0200 at 135° . $\text{H}_2\text{O}=4.71$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C}=12.31$; $\text{H}=0.85$;

$\text{H}_2\text{O}=4.61$ per cent.

Solubility.—One hundred grams of water dissolve 0.64 gram of the anhydrous salt at 16.5° .

The *potassium* salt, crystallising in fine, white needles, contains one molecule of water:

0.1458 gave 0.0660 CO_2 and 0.0088 H_2O . $\text{C}=12.34$; $\text{H}=0.66$.

0.4877 lost 0.0163 at 140° . $\text{H}_2\text{O}=3.34$.

0.2111 gave 0.0309 K_2SO_4 . $\text{K}=6.55$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}, \text{H}_2\text{O}$ requires $\text{C}=12.16$; $\text{H}=0.67$; $\text{H}_2\text{O}=3.04$;
 $\text{K}=6.58$ per cent.

Solubility.—One hundred grams of water dissolve 0.31 gram of the anhydrous salt at 14° .

The *ammonium* salt crystallises in small, yellow, anhydrous nodules.

Solubility.—One hundred grams of water dissolve 0.82 gram at 11° .

2 : 3 : 5-Tri-iodobenzenesulphonic Acid.

Ethyl 2 : 3 : 5-tri-iodobenzenesulphonate separates from a mixture of alcohol and ether in crystals of definite form, somewhat resembling those of copper sulphate; under certain conditions, which have not been definitely fixed, long needles are sometimes obtained; the needles on re-resolution in alcohol are changed into crystals of the other form. Both forms melt at 110° , and give identical analytical numbers:

First set (*needles*): 0.1370 gave 0.0849 CO_2 and 0.0167 H_2O .
 $\text{C}=16.91$; $\text{H}=1.35$.

Second set: 0.1867 gave 0.1168 CO_2 and 0.0211 H_2O . $\text{C}=17.06$;
 $\text{H}=1.25$.

$\text{C}_8\text{H}_7\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=17.02$; $\text{H}=1.24$ per cent.

Methyl 2 : 3 : 5-tri-iodobenzenesulphonate crystallises from a mixture of methyl alcohol and ether in long, transparent needles, melting at 137° :

0.1650 gave 0.0930 CO_2 and 0.0150 H_2O . $\text{C}=15.33$; $\text{H}=1.00$.

$\text{C}_7\text{H}_5\text{O}_3\text{I}_3\text{S}$ requires $\text{C}=15.27$; $\text{H}=0.91$ per cent.

The *sodium* salt probably crystallises with one molecule of water:

0.1531 gave 0.0697 CO_2 and 0.0100 H_2O . $\text{C}=12.41$; $\text{H}=0.71$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SNa}, \text{H}_2\text{O}$ requires $\text{C}=12.50$; $\text{H}=0.69$ per cent.

Solubility.—One hundred grams of water dissolve 0.55 gram of salt at 18° .

The *potassium* salt separates from water in small, glistening crystals containing one molecule of water:

0.2234 gave 0.1021 CO_2 and 0.0155 H_2O . $\text{C}=12.46$; $\text{H}=0.76$.

0.4643 lost 0.0144 at 150° . $\text{H}_2\text{O}=3.10$.

$\text{C}_6\text{H}_2\text{O}_3\text{I}_3\text{SK}, \text{H}_2\text{O}$ requires $\text{C}=12.16$; $\text{H}=0.67$;
 $\text{H}_2\text{O}=3.04$ per cent.

Solubility.—One hundred grams of water dissolve 0.139 gram of the anhydrous salt at 18°.

The *ammonium* salt is anhydrous. One hundred grams of water contain 0.69 gram at 18°.

Ethyl 2: 5-di-iodobenzenesulphonate crystallises from a mixture of ether and alcohol in long, stout needles, melting at 120.5°:

0.1740 gave 0.1411 CO₂ and 0.0296 H₂O. C=22.11; H=1.89.

C₈H₈O₃I₂S requires C=21.92; H=1.83 per cent.

Methyl 2: 5-di-iodobenzenesulphonate crystallises from alcohol in fine, woolly needles, melting at 106°:

0.0958 gave 0.0693 CO₂ and 0.0112 H₂O. C=19.72; H=1.29.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

Ethyl 3: 4-di-iodobenzenesulphonate separates from alcohol in needles, melting at 82.5°:

0.1851 gave 0.1483 CO₂ and 0.03 H₂O. C=21.85; H=1.79.

C₈H₈O₃I₂S requires C=21.92; H=1.83 per cent.

Methyl 3: 4-di-iodobenzenesulphonate crystallises from methyl alcohol in glistening cubes (?), melting at 93°:

0.1937 gave 0.1414 CO₂ and 0.0262 H₂O. C=19.90; H=1.49.

C₇H₆O₃I₂S requires C=19.81; H=1.41 per cent.

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XXIV.—A Natural Substantive Dyestuff.

By ARTHUR GEORGE PERKIN.

SOME time ago a small sample of an Egyptian natural dyestuff was received from the authorities of the Imperial Institute, under the name of the "red dura" of the Soudan, the dyeing properties of which proved to be specially interesting in that good shades upon wool could be obtained from it without the aid of a mordant. The material consisted of the leaf sheaths of a grass, smooth externally, possessing a deep reddish-brown tint, and approximately nine inches in length, together with cylindrical fragments of the stem (or pith) of a brighter, although feebler, colour. The following account of this plant was furnished by Mr. C. P. Browne, Inspector of the Blue Nile Province: "I attach a specimen of 'Sikhytan,' the species of durra used for producing a red dye, practically utilised for staining a grass called 'lanzura,' used in the

manufacture of coloured 'bursh' (mats), but occasionally for the leather of 'markubs' (Sudanese shoes). This durra is specially grown for the purpose and not for eating. It occurs in this district, but comes mainly from Rahad, Dinder, and the south." The results of the examination of this product at the Royal Botanic Gardens, Kew, indicated that it was apparently part of the stem, including the leaf sheaths, of the *Andropogon sorghum*, var. *vulgaris*, and this was interesting because this plant, also known as the *Sorghum vulgare*, constitutes the "Great Millet," the grain of which is so important a foodstuff. An elaborate account of the *Sorghum vulgare* is given by Watt ("Dictionary of the Economic Products of India," Vol. 6, Part III, p. 289), and it is worthy of note that in certain cases the grain is described as possessing a brick-red colour, and that at Harihar this is used for preparing a red morocco from goat skin. Again, it is stated in connexion with the *Sorghum saccharatum* that when the pressed canes are allowed to ferment, their colour changes to a red or reddish-brown, and that the dye thus produced can be extracted by means of dilute alkali, and is precipitated from this solution by means of acid in the form of red flakes. The Indian, Persian, Abyssinian, and Egyptian forms would seem to be derived from the *Andropogon sorghum*, var. "durrha" (*ibid.*, p. 278), but the fact that this plant is so extensively cultivated in Egypt as a foodstuff, whereas, according to Browne (*loc. cit.*), the "Sikhytan" is grown entirely on account of its dyeing properties, leaves one to infer that this latter is again a special variety. Unfortunately, but a few ounces of this material were available for examination, and this did not permit of any extended investigation of the colouring matter which is present, but should it be possible to obtain a large quantity of this dyestuff, a more exhaustive study of the subject will then be carried out.

EXPERIMENTAL.

The leaf sheaths and stems (pith) were examined separately, but as experiment showed that the same products were present in both cases, this was evidently not necessary. The material was extracted in a Soxhlet apparatus with boiling acetone until nothing further dissolved, and by evaporating the deep brownish-coloured extract there was obtained from the sheaths 16·27 per cent., and from the pith 14·7 per cent., of a dark brittle resin. On agitating this residue with cold acetone, a small quantity of substance did not pass into solution, and the operation was repeated until the final product was entirely soluble under this treatment. The amorphous substance thus removed, and which, when dry, possessed a slight beetle-green lustre, on incineration yielded some quantity

of ash, and appeared to consist of a calcium salt of the colouring matter. The partly evaporated acetone extract, on treatment with a little boiling benzene, deposited a dull ochre-coloured precipitate almost devoid of tinctorial property, which was removed and the filtrate fractionally evaporated. By this means a gradual separation of the colouring matter was effected, the earlier fractions possessing a deep maroon colour, and those obtained later having a beautiful scarlet tint. The final mother liquid contained, together with some quantity of plant wax, a trace of a yellow, resinous compound.

The crude colouring matter redissolved in a mixture of acetone and benzene was again fractionally crystallised as before, the first and final deposits being rejected, and this appeared to be the only method available in dealing with so small a quantity of the substance. The product consisted of a bright red, almost scarlet, powder, which under the microscope appeared as nodules possessing fine, saw-like edges, and thus possessed an ill-defined crystalline structure. The quantity of colouring matter thus isolated was approximately 3 grams, and of this four distinct preparations, dried at 160° , were analysed:

Found, C = 67.27; 67.53; 67.66; 67.40; H = 4.40; 4.61; 4.73; 4.33.

$C_{16}H_{12}O_5$ requires C = 67.60; H = 4.23 per cent.

It is very readily soluble in alcohol, very sparingly so in boiling water, and dissolves in alkaline solutions with a violet-red colour, which rapidly becomes brown owing to oxidation. It is only partly precipitated by excess of alcoholic lead acetate, forming a dull reddish-violet lake soluble in water, but is completely deposited by means of the basic acetate with formation of an insoluble lead salt. With alcoholic ferric chloride it gives a brown coloration, and its solution in both sulphuric and nitric acid is yellow, the latter acid reacting to form a nitro-compound precipitated by water. It does not contain methoxy-groups.

The colouring matter was fused with potassium hydroxide and a little water to $200-220^{\circ}$ for twenty minutes, the brownish-coloured mass dissolved in water, and the solution acidified and extracted with ether. The crystalline residue obtained by evaporating the ether, when examined in the usual way, gave phloroglucinol (m. p. 210°) and an acid, melting at 210° , which had all the properties of *p*-hydroxybenzoic acid, and could be admixed with it without alteration of melting point. A second experiment gave also a trace of a compound of lower melting point resembling *p*-hydroxyacetophenone, but this point requires further corroboration.

Merely a trace of the substance was available for dyeing experiments, but this was sufficient to indicate that the tinctorial

properties of the plant were entirely due to this colouring matter. As was to be expected from its behaviour with lead acetate solution, it does not dye mordanted calico, although, as previously indicated, it is a substantive dyestuff towards wool. By the use of a boiling aqueous extract of the plant itself, a dull red shade was obtained with woollen cloth, and this became rather weaker when it was treated with warm dilute soap solution. A very permanent and slightly fuller colour was produced by previously mordanting the wool with chromium or copper, and a similar result could be obtained by an application of the mordant after the dyeing operation. In comparison with the better-known substantive natural dyestuffs, the "red dura" very closely resembles in this behaviour the "insoluble red woods," which contain as the chief colouring matter santalin, and of which sanderswood (*Pterocarpus santalinus*) is a typical example. The shades given by the latter, although of a faintly yellower character, closely resemble those produced by the "red dura," and although the sanderswood possessed somewhat the stronger dyeing power, there was but a trifling distinction to be observed in this respect. Again, it was ascertained that by submitting sanderswood to a similar process to that described above, the colouring matter thus isolated was very similar in appearance and general properties to that obtained from the "red dura." It therefore seems appropriate to term this latter *dura-santalin*.

The formula of santalin, $C_{14}H_{11}O_4(O\cdot CH_3)$ (Cain and May, *J. Soc. Chem. Ind.*, 1909, **28**, 697), does not suggest the existence of a simple chemical relationship between these colouring matters, but it seems likely that they may possess in common a special grouping which will account for their close resemblance.

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LEEDS.

XXV.—The Effect of Contiguous Unsaturated Groups on Optical Activity. Part IV. Conjugated Systems containing more than Two Unsaturated Groups.

By SYDNEY ROBERT EDMINSON and THOMAS PERCY HILDITCH.

In the course of work on the effect of two adjacent unsaturated radicles on molecular rotatory power, some of which has already been published in earlier parts of this series, it has been established that a pronounced

increase of optical activity invariably accompanies the conjunction of two such groups. At the same time, it has frequently been noticed that when a third group, possessing marked residual affinity, happens to occur in close proximity to the studied systems, the increase in rotatory power is not always maintained, and, indeed, is sometimes markedly lessened.

This may be instanced from the menthyl esters of piperic and sorbic acids, recently studied by one of us (*Trans.*, 1909, **95**, 1570), of which we reproduce here the molecular rotatory powers and corresponding differences from the "normal value" of a menthyl ester (a quantity the approximate estimation of which has already been explained, *loc. cit.*, p. 1571):

	$[M]_D^{16}$.	Difference.
$C_6H_5 \cdot CH:CH \cdot CH:CH \cdot CO_2 \cdot C_{10}H_{19}$	-188.8	+28.3
$CH_3 \cdot CH:CH \cdot CH:CH \cdot CO_2 \cdot C_{10}H_{19}$	-221.3	+56.7

The brucine salts of these acids, on the other hand, show a "difference" of +218.8° for the piperate, and +119.5° for the sorbate, under identical polarimetric conditions.

Again, the brucine salts of anthranilic and salicylic acids and their acylated derivatives give evidence of similar irregularities (*Trans.*, 1908, **93**, 1388):

	$[M]_D$.	Difference.
Brucine benzoate	-131.1	+118.4
„ anthranilate	-47.8	+201.7
„ acetylanthranilate	+29.8	+279.3
„ benzoylanthranilate.....	+156.2	+405.7
„ benzoate	-131.1	+118.4
„ salicylate	+75.5	+325.0
„ acetylsalicylate.....	+86.7	+336.2
„ benzoylsalicylate	± 0.0	+249.5

Since mono-aryl esters of camphoric acid and camphor- β -sulphonic acid can be readily prepared and obtained pure, and since phenolic substances containing as many as five adjacent unsaturated groups are also easily obtainable, we thought it might prove interesting to examine as extended a series as possible of these derivatives. Difficulties appeared, however, in the case of the more complicated phenols used, chiefly owing to the decreasing facility of reaction shown on ascending the series, and to the anticipated fact that the higher esters, although not so strongly coloured as their parent phenols, began to be sufficiently dark yellow to interfere with polarimetric accuracy.

We have endeavoured to arrive at a "normal value" for the molecular rotatory power of acid esters of camphoric acid and of camphor- β -sulphonic esters, in accordance with the usual rule (*Tschugaeff, Ber.*, 1898, **31**, 360; *Walden, Ber.*, 1905, **38**, 355), by examining the methyl, ethyl, *n*-propyl, and *n*-butyl esters of the two acids. In the case of camphor- β -sulphonic acid, we did not succeed

in obtaining the propyl and butyl compounds in the pure state, and we have therefore used the molecular rotatory power of the ethyl ester as a basis of comparison, since it is well known that the first member of the series is almost always irregular.

We will return to a discussion of the polarimetric results after giving some account of the compounds studied.

EXPERIMENTAL.

The alkyl hydrogen camphorates were prepared according to J. Walker's directions (*Trans.*, 1892, **61**, 1088); a quantity of sodium being dissolved in excess of the respective alcohol, the equivalent amount of camphoric anhydride was added, and the mixture boiled for half an hour. The ester was then readily isolated from the sodium salt formed.

Brühl (*Ber.*, 1891, **24**, 3409) has observed that ethyl hydrogen camphorate tends to decompose, on being distilled in a vacuum, into the diethyl ester and camphoric anhydride. We invariably found traces of anhydride in the distillate (under a pressure of 20 mm.) from either the ethyl, *n*-propyl, or *n*-butyl hydrogen esters, and ultimately we purified them by extracting the ethereal solution of the crude product with aqueous sodium hydrogen camphorate. This extract was cooled to 0°, acidified with a slight excess of mineral acid, and extracted again with ether. The dried ethereal extract was filtered, the ether removed by distillation, and the residue heated on the water-bath in a vacuum for two hours. No appreciable decomposition thus took place, and the ethyl hydrogen ester so obtained showed a slightly higher rotation than that hitherto observed.

We should mention that Walker (*loc. cit.*) has proved that in the action of sodium alkyloxides on camphoric anhydride no *allo*-esters are formed.

Methyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Me}$.—Colourless needles, m. p. 77°:

0.1046 gave 0.2373 CO_2 and 0.0813 H_2O . C = 61.87; H = 8.64.

$\text{C}_{11}\text{H}_{18}\text{O}_4$ requires C = 61.69; H = 8.41 per cent.

Ethyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2\text{Et}$.—A colourless, viscous oil:

0.1004 gave 0.2344 CO_2 and 0.0788 H_2O . C = 63.66; H = 8.72.

$\text{C}_{12}\text{H}_{20}\text{O}_4$ requires C = 63.17; H = 8.77 per cent

n-Propyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2 \cdot \text{C}_3\text{H}_7$.—A colourless, viscous oil:

0.1040 gave 0.2456 CO_2 and 0.0846 H_2O . C = 64.40; H = 9.04.

$\text{C}_{13}\text{H}_{22}\text{O}_4$ requires C = 64.46; H = 9.09 per cent.

n-Butyl hydrogen camphorate, $\text{CO}_2\text{H}\cdot\text{C}_8\text{H}_{14}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$.—A colourless oil, much more limpid than the two preceding:

0.1866 gave 0.4525 CO_2 and 0.1516 H_2O . $\text{C} = 66.18$; $\text{H} = 9.03$.

$\text{C}_{14}\text{H}_{24}\text{O}_4$ requires $\text{C} = 65.63$; $\text{H} = 9.38$ per cent.

The alkylcamphor- β -sulphonates were obtained by heating equivalent amounts of sodium alkyloxide and camphor- β -sulphonyl chloride in the respective alcohols for a short time. The product was mixed with ice-water, and, when it had completely solidified, it was collected and recrystallised from aqueous methyl alcohol.

Methyl camphor- β -sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\text{Me}$.—Soft, white needles, melting at 61° :

0.1041 gave 0.2046 CO_2 and 0.0664 H_2O . $\text{C} = 53.60$; $\text{H} = 7.09$.

0.1630 „ 0.1524 BaSO_4 . $\text{S} = 12.83$.

$\text{C}_{11}\text{H}_{18}\text{O}_4\text{S}$ requires $\text{C} = 53.67$; $\text{H} = 7.32$; $\text{S} = 13.01$ per cent.

Ethyl camphor- β -sulphonate, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\text{Et}$.—Wax-like plates, melting at 47° :

0.1064 gave 0.2156 CO_2 and 0.0750 H_2O . $\text{C} = 55.25$; $\text{H} = 7.83$.

$\text{C}_{12}\text{H}_{20}\text{O}_4\text{S}$ requires $\text{C} = 55.39$; $\text{H} = 7.69$ per cent.

The *n*-propyl and *n*-butyl esters were not obtained solid, either by crystallisation from a number of solvents or on standing in a vacuum desiccator for several weeks, and they were therefore not examined.

The unsaturated compounds studied may be divided into those derived from phenol (*o*-hydroxybenzylidene-acetone and -acetophenone) and from the naphthols (2-aceto- and 2-benzo-*a*-naphthol) respectively. The latter substances were prepared by heating 10 grams of *a*-naphthol with 15 grams of zinc chloride and 20 grams of acetic or benzoic acid at 150° for half an hour (Friedländer, *Ber.*, 1895, 28, 1946). Friedländer has characterised 2-aceto-*a*-naphthol, and shown it to possess the assigned structure, but the similarly formed 2-benzo-*a*-naphthol does not seem to have been described.

It is obtained in the form of a yellow, amorphous, partly hydrolysed sodium salt on pouring the cold reaction product (see above) into dilute aqueous sodium carbonate; from this salt the phenol itself can be isolated as a yellow, crystalline solid, melting, after recrystallisation from dilute alcohol, at 77° :

0.1039 gave 0.3123 CO_2 and 0.0486 H_2O . $\text{C} = 82.00$; $\text{H} = 5.20$.

$\text{C}_{17}\text{H}_{12}\text{O}_2$ requires $\text{C} = 82.24$; $\text{H} = 4.84$ per cent.

The *benzoyl* derivative, prepared by the Schotten-Baumann method, crystallises from light petroleum in pale yellow leaflets, melting at 154° to a dark red liquid:

0.1326 gave 0.3969 CO₂ and 0.0528 H₂O. C=81.68 ; H=4.43.

C₂₄H₁₆O₈ requires C=81.83 ; H=4.55 per cent.

2-*Benzo-α-naphthol* displays a great tendency to form insoluble salts with bases ; the pale yellow, amorphous *sodium* and *ammonium* salts, and the yellow, crystalline *piperidine* salt, melting at 138°, are all partly hydrolysed by cold water, but the still less soluble, brownish-yellow *barium* salt is much more stable :

0.2571 gave 0.0957 BaSO₄. Ba=21.91.

C₃₄H₂₂O₄ Ba requires Ba=21.71 per cent.

The phenolic hydrogen camphorates were obtained according to Schryver's method (Trans., 1899, 75, 661) ; since, however, it appeared that his directions for preparing the phenolic sodium salts might in some of the present cases give rise to secondary reactions, owing to the presence of metallic sodium, these were prepared by adding the equivalent amount of sodium ethoxide to the phenol in alcohol. After evaporating the alcohol and drying the sodium salt in a vacuum on the water-bath, xylene and the requisite amount of camphoric anhydride were added. With some of the more complex phenols, too prolonged heating appeared to give rise to by-products, a maximum, although frequently not very satisfactory, yield being obtained after heating at 100° for about half-an-hour.

Phenyl hydrogen camphorate, CO₂H·C₈H₁₄·CO₂Ph.—Slender needles from methyl alcohol, melting at 98° (100° : Schryver) :

0.1217 gave 0.3096 CO₂ and 0.0815 H₂O. C=69.38 ; H=7.49.

C₁₆H₂₀O₄ requires C=69.56 ; H=7.25 per cent.

o-β-Acetylvinylphenyl hydrogen camphorate,

CO₂H·C₈H₁₄·CO₂·C₆H₄·CH:CHAc.

—Soft, yellow plates from alcohol, decomposing at 111° :

0.1948 gave 0.5006 CO₂ and 0.1237 H₂O. C=70.08 ; H=7.05.

C₂₀H₂₄O₅ requires C=69.76 ; H=6.98 per cent.

o-β-Benzoylvinylphenyl hydrogen camphorate,

CO₂H·C₈H₁₄·CO₂·C₆H₄·CH:CHBz,

was not obtained in very good yield ; it forms yellow crystals from benzene by precipitation with light petroleum. The compound, which was rather easily hydrolysed, melted at 145° :

0.1104 gave 0.2961 CO₂ and 0.0606 H₂O. C=73.38 ; H=6.10.

C₂₅H₂₆O₅ requires C=73.89 ; H=6.40 per cent.

β-Naphthyl hydrogen camphorate, CO₂H·C₈H₁₄·CO₂·C₁₀H₇.—Pure white crystals from aqueous alcohol, melting at 125° (121—122° : Schryver) :

0.1128 gave 0.3073 CO₂ and 0.0740 H₂O. C=74.10 ; H=7.29.

C₂₀H₂₂O₄ requires C=73.62 ; H=6.75 per cent.

α-Naphthyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_7$.—White prisms, which melted somewhat indefinitely at about 170° :

0.1172 gave 0.3163 CO_2 and 0.0734 H_2O . $\text{C} = 73.58$; $\text{H} = 6.96$.

$\text{C}_{20}\text{H}_{22}\text{O}_4$ requires $\text{C} = 73.62$; $\text{H} = 6.75$ per cent.

2-Aceto-α-naphthyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_6\text{Ac}$.—White needles, melting at 102° :

0.1444 gave 0.3815 CO_2 and 0.0858 H_2O . $\text{C} = 72.05$; $\text{H} = 6.60$.

$\text{C}_{22}\text{H}_{24}\text{O}_5$ requires $\text{C} = 71.74$; $\text{H} = 6.52$ per cent.

2-Benzo-α-naphthyl hydrogen camphorate, $\text{CO}_2\text{H} \cdot \text{C}_8\text{H}_{14} \cdot \text{CO}_2 \cdot \text{C}_{10}\text{H}_6\text{Bz}$.—A yellow, crystalline powder from benzene, melting and decomposing at 172° :

0.1059 gave 0.2924 CO_2 and 0.0572 H_2O . $\text{C} = 75.30$; $\text{H} = 6.05$.

$\text{C}_{27}\text{H}_{26}\text{O}_5$ requires $\text{C} = 75.34$; $\text{H} = 6.05$ per cent.

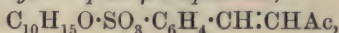
The corresponding camphor- β -sulphonates were all prepared by the Schotten-Baumann method, using very dilute aqueous sodium hydroxide and maintaining the reaction solution at such a temperature that the camphor- β -sulphonyl chloride always remained a little above its point of fusion.

Phenyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3\text{Ph}$, only solidified after standing some time in a vacuum, but thereafter crystallised from light petroleum in long, radiating, colourless needles, melting at 48° :

0.1055 gave 0.2414 CO_2 and 0.0610 H_2O . $\text{C} = 62.38$; $\text{H} = 6.42$.

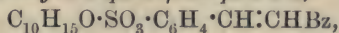
$\text{C}_{16}\text{H}_{20}\text{O}_4\text{S}$ requires $\text{C} = 62.32$; $\text{H} = 6.49$ per cent.

o-β-Acetylvinyphenyl camphor-β-sulphonate,



was found to be a yellow oil, which would not crystallise, and, as no other means of purification besides crystallisation existed, it could not be utilised.

o-β-Benzoylvinyphenyl camphor-β-sulphonate,



crystallising in yellow needles from benzene, melted at 102° :

0.1000 gave 0.2497 CO_2 and 0.0548 H_2O . $\text{C} = 68.10$; $\text{H} = 6.09$.

$\text{C}_{25}\text{H}_{26}\text{O}_5\text{S}$ requires $\text{C} = 68.48$; $\text{H} = 5.94$ per cent.

β-Naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3 \cdot \text{C}_{10}\text{H}_7$, crystallised in faintly pink prisms from aqueous alcohol, and melted at 100° :

0.0978 gave 0.2396 CO_2 and 0.0549 H_2O . $\text{C} = 66.82$; $\text{H} = 6.24$.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}$ requires $\text{C} = 67.04$; $\text{H} = 6.15$ per cent.

α-Naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3 \cdot \text{C}_{10}\text{H}_7$.—White needles from dilute alcohol, melting at 109° :

0.1097 gave 0.2697 CO_2 and 0.0624 H_2O . $\text{C} = 67.04$; $\text{H} = 6.32$.

$\text{C}_{20}\text{H}_{22}\text{O}_4\text{S}$ requires $\text{C} = 67.04$; $\text{H} = 6.15$ per cent.

2-Aceto-α-naphthyl camphor-β-sulphonate, $\text{C}_{10}\text{H}_{15}\text{O} \cdot \text{SO}_3 \cdot \text{C}_{10}\text{H}_6\text{Ac}$.—

Small, hard, cream-coloured needles from alcohol, which melted at 102° :

0.1039 gave 0.2510 CO_2 and 0.0546 H_2O . $\text{C} = 65.90$; $\text{H} = 5.84$.

$\text{C}_{22}\text{H}_{24}\text{O}_5\text{S}$ requires $\text{C} = 66.00$; $\text{H} = 6.00$ per cent.

2-Benzo- α -naphthyl camphor- β -sulphonate was not obtained in the solid state, and therefore had to be omitted from the series.

The polarimetric observations were carried out exactly as in previous investigations of this series, the temperature being maintained at 23° . For the alkyl esters, the following values were obtained:

Chloroform solutions:		5 per cent.		2½ per cent.	
		$[\alpha]_{\text{D}}$	$[M]_{\text{D}}$	$[\alpha]_{\text{D}}$	$[M]_{\text{D}}$
Methyl hydrogen camphorate	...	+57.71	+123.5	+58.50	+125.2
Ethyl	"	38.72	88.3	39.80	90.7
n-Propyl	"	38.76	93.8	38.56	93.3
n-Butyl	"	35.60	91.1	36.24	92.8
Mean $[M]_{\text{D}}^{23^{\circ}}$ (ethyl n-butyl)			91.1		92.3
Methyl camphor- β -sulphonate	...	+43.61	+107.3	+43.40	+106.8
Ethyl	"	43.91	114.2	43.28	112.6

In certain instances it was found impossible to obtain an accurate reading with the 5 per cent. solutions of the phenolic esters, and therefore, especially as in none of the other cases was there any marked change of rotatory power on dilution, we give only the values measured in 2.5 per cent. chloroform solution; the numbers obtained by one of us (*loc. cit.*) for the *o*-tolyl and *o*-aldehydophenyl esters are incorporated in the table.

	Hydrogen camphorate.			Camphor- β -sulphonate.		
	$[\alpha]_{\text{D}}$	$[M]_{\text{D}}$	Diff.	$[\alpha]_{\text{D}}$	$[M]_{\text{D}}$	Diff.
{ Phenyl	+45.38	+125.2	+32.9	+40.56	+124.9	+12.3
{ <i>o</i> -Tolyl	45.0	130.5	38.2	46.0	148.1	35.5
{ <i>o</i> -Aldehydophenyl.....	48.1	146.2	53.9	39.6	133.1	20.5
{ <i>o</i> -Acetylvinylphenyl...	30.04	103.3	12.2	—	—	—
{ <i>o</i> - β -Benzoylvinylphenyl	49.44	200.7	108.4	27.2	119.1	6.5
{ β -Naphthyl	53.28	173.7	81.4	30.16	108.0	-4.6
{ α -Naphthyl	34.24	111.6	19.3	38.24	137.0	+24.4
{ 2-Aceto- α -naphthyl ...	38.00	139.8	47.5	50.02	200.1	87.5
{ 2-Benzo- α -naphthyl ...	52.82	227.2	134.9	—	—	—

There are thus included in the above summary four groups of substances, namely, hydrogen camphorates of the phenyl and of the naphthyl series, and camphor- β -sulphonates of the same. Of these, the two first-mentioned show a steady increase of rotatory power with the increasing number of conjugated groups, but the camphor- β -sulphonic series is, to all appearances, perfectly irregular. These results are further confused by the isomeric α - and β -naphthyl compounds, where there is a very notable difference of rotation in both the camphoric and the camphor- β -sulphonic series, but in conflicting directions.

We will refer, in conclusion, to three other series of this type of compounds, which would seem to exhaust all the available data; the first comprises the camphorates of certain aromatic amines, compared with di-*n*-butylamine camphorate ($[M]_D^{20^\circ}$ 38.6 in 2.5 per cent. chloroform solution):

	$[M]_D$	Difference.
Di- <i>p</i> -toluidine camphorate	+ 99.4	+ 60.8
Di- <i>p</i> -aminoacetophenone camphorate.	91.2	52.6
Di- <i>p</i> -aminobenzophenone camphorate	73.6	35.0

Next, there are certain condensation products of camphor with aromatic aldehydes:

	$[M]_D$			$[M]_D$
Benzylidenecamphor *	+ 1020		Benzylcamphor *	+ 348
Cinnamylidenecamphor † ...	788		γ -Phenylpropylcamphor †	178

* Haller, *Compt. rend.*, 1899, 128, 1370.

† Rupe and Frisell, *Ber.*, 1905, 38, 104.

And, finally, certain esters recently examined by Rupe (*Annalen*, 1909, 369, 311):

	$[M]_D^{20^\circ}$	Difference.
Menthyl diphenylacetate	- 233.4	+ 75.6
„ α -phenylcinnamate	193.5	+ 35.7
„ β -phenylcinnamate	137.3	- 21.5

Rupe draws the empirical conclusion that a phenyl group in the nearest possible position to the asymmetric system enhances rotatory power, but in others, further removed, depresses it; it appears not a little remarkable that one and the same group should exert a strong influence in two opposing directions, according as it is united with the α - or γ -carbon atoms.

We may summarise these data by pointing out that of the eleven series to which we have referred, four show a steady increase, four show a decrease, and the remaining three manifest indefinite changes in optical activity on increasing beyond two the number of contiguous unsaturated systems. Sufficient facts for a profitable discussion as to whether the indefinite numbers result from conflicting influences other than that due to conjugation, or whether the regular series are simply coincidences, appears still to be lacking.

It will be observed that the difference between the esters of even such nearly related bodies as phenol and *o*-cresol are considerable, and one cause of irregularity may lie in the fact that most of the esters studied above are the earlier members of homologous series, and may thus be abnormal, as has so frequently been noticed in the first members of other series. There is, indeed, little doubt that interesting and more comparable results would follow from a study of active esters of, for example, one of the higher normal aliphatic alcohols, replacing successive methylene groups by a system of multiple,

identical unsaturated groups, but such a series would be very difficult to prepare.

We desire to offer our hearty thanks to Professor Knorr, in whose laboratory this work has been carried out.

UNIVERSITY OF JENA.

XXVI.—*The Constituents of Red Clover Flowers.*

By FREDERICK BELDING POWER and ARTHUR HENRY SALWAY.

THE flowers of the common red clover (*Trifolium pratense*, Linné) have been used to some extent medicinally in recent years on account of their assumed alterative properties, and have even been recommended in the treatment of cancer (*Amer. J. Pharm.*, 1881, **53**, 85). So far as known to us, these flowers have never been subjected to a chemical examination, and the only knowledge of their constituents appears to be embodied in a statement that they contain tannin, two resins, fat, and chlorophyll. In this connexion it may incidentally be noted that Perkin and Phipps, in a paper entitled "Notes on some Natural Colouring Matters" (*Trans.*, 1904, **85**, 58), have recorded that a cursory examination of the flowers of the white clover (*Trifolium repens*) indicated the presence of quercetin in the form of a glucoside. The same authors furthermore remark that "this colouring matter was recognised by the melting point of its acetyl derivative, and its decomposition products with caustic alkali, and in consequence of these observations a fuller investigation appeared unnecessary."

In view of the above considerations, and the fact that red clover flowers are available in practically unlimited quantities, it appeared desirable that a complete study of their constituents should be undertaken. The present investigation has disclosed the presence of a considerable number of new and interesting substances, and a summary of the results obtained is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation was carefully collected for us under the superintendence of Mr. P. E. F. Perrédès, B.Sc., F.L.S., during the month of June, from a field of cultivated red clover (*Trifolium pratense*, Linné) in Kent. The flowers or blossoms were separately gathered, and were therefore, so far as possible, free from the green, herbaceous parts of the plant.

A portion (10 grams) of the dried flowers was tested for an alkaloid, but the reactions obtained were so slight as to indicate the presence of not more than traces of such a substance.

A further portion (25 grams) of the dried flowers was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried in a water-oven, were obtained:

Petroleum (b. p. 35—50°) extracted	0.50 gram	=	2.0 per cent.
Ether	0.50 "	=	2.0 "
Chloroform	0.35 "	=	1.4 "
Ethyl Acetate	1.50 "	=	6.0 "
Alcohol	4.50 "	=	18.0 "
<hr/>			
Total	7.35 grams	=	29.4 per cent.

For the purpose of a complete examination, 264 kilograms of the flowers were collected. This material, after careful drying, amounted to 58.5 kilograms, or 22.16 per cent. of the original weight. The entire amount of this material was coarsely powdered, and then extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, which was conducted at a temperature not exceeding 85°, a dark green, viscid extract was obtained, which amounted to 15.78 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

A quantity (1.5 kilograms) of the above-mentioned extract was brought into a suitable apparatus with a little water, and steam passed through the mixture for several hours. The distillate, which contained some oily drops, was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A small amount (1.5 grams) of an essential oil was thus obtained, which possessed a rather unpleasant odour. On subsequently treating 10 kilograms of the alcoholic extract in the manner above described, a further quantity (10.5 grams) of essential oil was obtained. The yield of oil was thus equivalent to 0.028 per cent. of the dried, or 0.006 per cent. of the fresh clover flowers. This essential oil, when distilled under diminished pressure, passed over between 90° and 160°/20 mm. as a light yellow liquid, which, however, on keeping, ultimately became reddish-brown, and was found to contain furfuraldehyde. It possessed the following constants: $d_{20}^{20} = 0.9476$; $n_D^{20} + 4.0'$ in a 1-dcm. tube.

Non-volatile Constituents of the Extract.

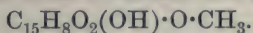
After the removal of the volatile constituents of the extract by distillation with steam, as above described, there remained in the

distillation flask a reddish-brown, aqueous liquid (A) and a quantity of a viscid resin (B), which became solid on cooling. The resin was collected, and thoroughly washed with water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid was concentrated under diminished pressure, and then repeatedly extracted with large volumes of ether. The ethereal extracts, which were of a light green colour, were united, washed with a little water, dried, and the ether removed, when 10 grams of a dark-coloured, soft solid were obtained. This was found by a preliminary examination to consist of a complex mixture of crystalline compounds, and, in order to obtain a quantity sufficient for their separation and characterisation, 10 kilograms of clover extract were treated as above described, the resulting aqueous liquid being extracted with ether. The yield of ethereal extract from this quantity of material was 64 grams.

Isolation of a New Phenolic Substance, Pratol,



The above-mentioned ethereal extract was digested with a quantity of ether insufficient to dissolve the whole, and the sparingly soluble portion, which amounted to 3 grams, separated by filtration. This product was repeatedly crystallised from alcohol, when a substance was obtained which separated in colourless needles, melting at 253° :

0.1265 gave 0.3307 CO_2 and 0.0513 H_2O . $\text{C} = 71.3$; $\text{H} = 4.5$.

0.1213 „ 0.3161 CO_2 „ 0.0500 H_2O . $\text{C} = 71.1$; $\text{H} = 4.6$.

$\text{C}_{16}\text{H}_{12}\text{O}_4$ requires $\text{C} = 71.6$; $\text{H} = 4.5$ per cent.

The above compound, when heated with acetic anhydride, yielded an *acetyl* derivative, which separated from alcohol in feathery needles, melting at 166° . This was analysed, and its molecular weight determined, with the following results:

0.1039 gave 0.2646 CO_2 and 0.0420 H_2O . $\text{C} = 69.5$; $\text{H} = 4.5$.

0.1069 „ 0.2715 CO_2 „ 0.0436 H_2O . $\text{C} = 69.3$; $\text{H} = 4.5$.

0.1485, in 33.26 of acetic acid, gave $\Delta t - 0.057^\circ$. $\text{M.W.} = 305$.

$\text{C}_{16}\text{H}_{11}\text{O}_4(\text{CO}\cdot\text{CH}_3)$ requires $\text{C} = 69.7$; $\text{H} = 4.5$ per cent. $\text{M.W.} = 310$.

The substance $\text{C}_{16}\text{H}_{12}\text{O}_4$ was found to contain one methoxyl group, as determined by Perkin's modification of the Zeisel method:

0.0995 gave 0.0785 AgI . $\text{MeO} = 10.4$.

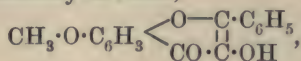
$\text{C}_{15}\text{H}_9\text{O}_3(\text{OMe})$ requires $\text{MeO} = 11.6$ per cent.

No compound of the formula $\text{C}_{16}\text{H}_{12}\text{O}_4$, possessing the same

properties as that above described, appears to have hitherto been recorded. It is therefore proposed to designate the substance from red clover flowers as *pratol*, with reference to its phenolic character and the specific botanical name of the plant.

Pratol, $C_{15}H_8O_2(OH) \cdot O \cdot CH_3$, crystallises in a very characteristic form, since it separates from alcohol in needles, which, under the microscope, are seen to have a talon-like shape with curved edges. It is moderately soluble in hot alcohol, but only sparingly soluble in water, ether, chloroform, or benzene. It dissolves readily in hot aqueous sodium carbonate and sodium hydroxide, yielding pale yellow solutions. When dissolved in acetic anhydride, and a drop of sulphuric acid added, a yellow coloration is produced. With ferric chloride no appreciable change of colour was observed.

Pratol is isomeric with several flavone derivatives, such as the 2-methoxy- and 3-methoxy-flavonol,



prepared by Kostanecki and his co-workers (*Ber.*, 1904, **37**, 775; 1905, **38**, 993). The general behaviour of *pratol* is also very similar to that of the above-mentioned substances, and it therefore seems probable that it represents one of the many hydroxymethoxy-flavones which are theoretically possible.

Acetylpratol, $C_{16}H_{11}O_4(CO \cdot CH_3)$, prepared, as above noted, by heating *pratol* with acetic anhydride, is very soluble in hot alcohol, but only moderately so in chloroform or benzene.

The ethereal liquid from which the sparingly soluble *pratol* had been separated by filtration, as above described, was subsequently shaken with an aqueous solution of ammonium carbonate (*a*) until nothing further was removed by this reagent, then with successive small portions of aqueous sodium carbonate (*b*), and finally with aqueous sodium hydroxide (*c*). These extracts were then separately examined.

Isolation of Salicylic Acid.

The liquids obtained by extraction with ammonium carbonate (*a*) were united, acidified with sulphuric acid, and extracted with ether. This ethereal liquid, on the removal of the solvent, yielded a quantity (20 grams) of a dark green oil. The latter was digested with considerable quantities of hot light petroleum, these liquids being decanted, and the solvent evaporated. In this manner 2 grams of colourless needles were obtained, which, after a few crystallisations from water, melted at 154° and gave an intense violet coloration with ferric chloride:

0.1230 gave 0.2765 CO_2 and 0.0507 H_2O . $\text{C}=61.3$; $\text{H}=4.6$.

$\text{C}_7\text{H}_6\text{O}_3$ requires $\text{C}=60.9$; $\text{H}=4.3$ per cent.

This substance was thus identified as salicylic acid.

The portion of the ammonium carbonate extract which was insoluble in light petroleum was heated for some time with methyl alcohol in the presence of concentrated sulphuric acid. A product was thus obtained which could be further separated into phenolic and non-phenolic methyl esters by shaking its ethereal solution with dilute aqueous sodium hydroxide. The portion insoluble in the alkaline liquid, consisting of the non-phenolic esters, amounted to 10 grams, and was a dark-coloured oil. It was hydrolysed with alcoholic potassium hydroxide, and the regenerated acids distilled under diminished pressure, when fractions were collected at $100\text{--}130^\circ$ and $130\text{--}230^\circ/20\text{ mm.}$, whilst a quantity of undistillable resin remained in the flask. These fractions were further examined by neutralising them with aqueous sodium carbonate, and fractionally precipitating the solutions with silver nitrate. A series of silver salts was thus obtained, which, with the exception of the last fraction (III), were more or less brown in colour. After drying in a vacuum over sulphuric acid, they were analysed:

Fraction $100\text{--}130^\circ/20\text{ mm.}$

0.1760 of salt gave 0.0852 Ag. Ag=48.4.

Fraction $130\text{--}230^\circ/20\text{ mm.}$

(I) 0.4969 of salt gave 0.1904 Ag. Ag=38.4.

(II) 0.1531 „ „ 0.0700 Ag. Ag=45.7.

(III) 0.7246 „ „ 0.4444 Ag. Ag=61.3.

It was evident from these results that the non-phenolic acids consisted of a complex mixture.

Identification of p-Coumaric Acid.

The portion of the above-mentioned methylated product which was soluble in aqueous sodium hydroxide was benzoylated by the Schotten-Baumann method, and then subjected to fractional crystallisation from alcohol. After a quantity of gummy, amorphous matter had been separated, a crystalline substance was deposited, which was ultimately obtained in slender needles, melting at 129° :

0.0783 gave 0.2079 CO_2 and 0.0390 H_2O . $\text{C}=72.4$; $\text{H}=5.5$.

$\text{BzO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{Me}$ requires $\text{C}=72.3$; $\text{H}=5.0$ per cent.

This compound is thus seen to agree in composition with the *benzoyl* derivative of *methyl p-coumarate*, which hitherto appears not to have been described. A little of it was therefore prepared for the purpose of comparison, when it was found to crystallise in

slender needles, melting at 129° , and to be identical in all respects with the compound obtained from the acid present in red clover flowers. The identity of the latter acid was further confirmed by the hydrolysis of the benzoyl derivative of its methyl ester, when a substance was obtained which crystallised from water in colourless needles, melting at 215° with evolution of carbon dioxide, and otherwise exhibited all the characters of *p*-coumaric acid.

Isolation of a New Yellow Compound, $C_{16}H_{10}O_7$.

The sodium carbonate extracts (*b*), obtained as above described, were separately acidified, and the resulting precipitates collected and examined. The product obtained from the first sodium carbonate extract consisted chiefly of chlorophyll, and nothing crystalline could be isolated from it. The second sodium carbonate extract yielded a yellow powder, which was dissolved in hot alcohol, in which it was freely soluble. This solution, after being kept for some time, deposited a small amount of a colourless, crystalline substance, which, after purification, melted at 253° , and yielded an acetyl derivative melting at 166° . It was found to be identical with the substance $C_{16}H_{12}O_4$, designated as pratol, which has already been described. As the mother liquors, which still contained all of the yellow compound, deposited nothing further on standing, the alcohol was completely removed, and the residue acetylated by means of acetic anhydride. On distilling off the greater part of the latter liquid, a crystalline product separated, which proved to be a mixture of substances. It was fractionally crystallised from alcohol, when a small quantity (1.0 gram) of an *acetyl* derivative was obtained, which appeared to be homogeneous, and separated in colourless, glistening, prismatic needles, melting at 145 — 147° with evolution of gas:

0.1530 gave 0.3347 CO_2 and 0.0555 H_2O . $C=59.7$; $H=4.0$.

The acetyl content of this compound was determined by heating it for some time with dilute sulphuric acid in the presence of alcohol, the alcohol being then completely removed, and the precipitated yellow substance, which was insoluble in cold water, collected and weighed:

0.1690 gave 0.1108 of yellow substance, or 65.6 per cent.

$C_{16}H_6O_7Ac_4$ requires $C=59.8$; $H=3.7$; $C_{16}H_{10}O_7=65.1$ per cent.

$C_{16}H_8O_7Ac_4$ „ $C=59.5$; $H=4.1$; $C_{16}H_{12}O_7=65.3$ „

It would appear from these results that the yellow compound possesses the formula $C_{16}H_{10}O_7$, and that it contains four hydroxyl groups. The presence of a methoxyl group was also established. The compound, $C_{16}H_{10}O_7$, as obtained from its acetyl derivative,

crystallises from boiling dilute alcohol in thin, yellow plates, which melt and decompose at about 280° . It is readily soluble in alcohol or acetic acid, but sparingly so in water, ether, chloroform, or benzene. It dissolves in alkalis with a yellow colour, and its solution in concentrated sulphuric acid exhibits a brilliant green fluorescence. In alcoholic solution it gives with ferric chloride a bluish-black coloration. The amount of this substance available was not sufficient for its further examination.

Isolation of a New Phenolic Substance, Pratensol, $C_{17}H_9O_2(OH)_3$.

The final sodium carbonate extract of the above-mentioned ethereal liquid yielded, on acidification, a light brown powder. This was dissolved in hot alcohol, and the solution kept for some time, when a small amount of the previously described pratol, $C_{16}H_{12}O_4$ (m. p. 253°), was deposited. The mother liquors from the latter contained a quantity of a very soluble substance, which could not be obtained directly in a crystalline form. The alcohol was therefore removed, and the residue acetylated, when a product was obtained which, after a few crystallisations from alcohol, yielded a pure, colourless *acetyl* derivative, melting at 189° :

0.1071 gave 0.2569 CO_2 and 0.0445 H_2O . $C=65.4$; $H=4.6$.

0.1002 „ 0.2410 CO_2 „ 0.0406 H_2O . $C=65.6$; $H=4.5$.

The molecular weight of the acetyl derivative was determined by the ebullioscopic method:

0.3518, in 25.62 of benzene, gave Δt 0.094° . M.W.=390.

$C_{23}H_{18}O_8$ requires $C=65.4$; $H=4.3$ per cent. M.W.=422.

The number of acetyl groups in this compound was ascertained by hydrolysing with aqueous sodium hydroxide, then adding a slight excess of sulphuric acid, and distilling the mixture in a current of steam:

0.2057 gave acetic acid equivalent to 14.45 c.c. $N/10$ -Ba(OH) $_2$.
 $CO \cdot CH_3 = 30.2$.

$C_{17}H_9O_5(CO \cdot CH_3)_3$ requires $CO \cdot CH_3 = 30.6$ per cent.

From these results it may be concluded that the substance contained in red clover flowers, from which the above-described tri-acetyl derivative was prepared, possesses the formula $C_{17}H_{12}O_5$. In order to obtain the parent compound, the acetyl derivative was heated for some time in alcoholic solution with dilute sulphuric acid, and the alcohol subsequently removed by distillation with steam, when a colourless, crystalline substance separated. This was purified by crystallisation from benzene, when it separated in feathery needles, melting at 210° . Although the amount of this substance was insufficient for analysis, it was proved to represent

the original compound by the fact that when again acetylated, it yielded an acetyl derivative melting at 189° .

No compound of the formula $C_{17}H_{12}O_5$, possessing the same properties as that above described, appears to have hitherto been recorded. It is therefore proposed to designate the substance contained in red clover flowers as *pratensol*, with reference to its phenolic character and the specific botanical name of the plant.

Pratensol, $C_{17}H_9O_2(OH)_3$, is very readily soluble in alcohol and acetic acid, but only sparingly soluble in water, chloroform, and benzene. It dissolves in alkali carbonates, yielding yellow solutions, whilst its alcoholic solution gives with ferric chloride a greenish-black coloration.

Triacetylpratensol, $C_{17}H_9O_5(CO \cdot CH_3)_3$, crystallises from alcohol, in which it is only moderately soluble, in colourless, slender needles. It is readily soluble in glacial acetic acid, and moderately soluble in benzene. When warmed with dilute aqueous sodium hydroxide, not only are the three acetyl groups removed, but the molecule also undergoes further change, with the formation of a compound which crystallises from dilute alcohol in long, colourless needles, melting at $183-184^{\circ}$. If, on the other hand, the acetyl compound is heated with aqueous sodium carbonate, the product is a yellow, crystalline substance, which melts and decomposes at 160° . It was not possible to ascertain the exact nature of these changes on account of the small amount of substance available, since 37.1 kilograms of dried clover flowers yielded not more than 1.5 grams, or about 0.004 per cent., of pure triacetylpratensol.

Isolation of a New Phenolic Substance, $C_{15}H_7O_3(OH)_3$.

The sodium hydroxide extracts (c) of the previously mentioned ethereal liquid, when acidified, yielded a light green powder, which possessed an odour resembling that of eugenol. An attempt to identify the latter by distilling the product with steam was, however, unsuccessful. The light green powder was subsequently decolorised by treating its hot alcoholic solution with animal charcoal, when, on cooling, colourless clusters of feathery needles separated. After several crystallisations, the substance was obtained pure, and then melted at 225° :

0.0931 gave 0.2133 CO_2 and 0.0310 H_2O . $C = 62.5$; $H = 3.7$.

$C_{15}H_{10}O_6$ requires $C = 62.9$; $H = 3.5$ per cent.

This compound yielded an *acetyl* derivative, which separated from alcohol in thin, silky needles, melting at 209° . The acetyl content of this compound was ascertained by hydrolysing with dilute aqueous sodium hydroxide, then acidifying with sulphuric acid, and distilling the mixture in a current of steam:

0.1750 gave acetic acid equivalent to 12.5 c.c. $N/10\text{-Ba(OH)}_2$.
 $\text{CO}\cdot\text{CH}_3=30.7$.

The molecular weight of the acetyl derivative was also ascertained by the ebullioscopic method:

0.1768, in 26.46 of benzene, gave Δt 0.043° . M.W.=415.
 $\text{C}_{15}\text{H}_7\text{O}_6(\text{CO}\cdot\text{CH}_3)_3$ requires $\text{CO}\cdot\text{CH}_3=31.3$ per cent. M.W.=412.

The substance, $\text{C}_{15}\text{H}_{10}\text{O}_6$, is soluble in alkali hydroxides, forming a colourless solution. In alcoholic solution it gives with ferric chloride a dark green coloration. With concentrated sulphuric acid, only a faint yellow colour is produced.

The yield of the substance $\text{C}_{15}\text{H}_{10}\text{O}_6$ was very small, not more than 0.5 gram having been obtained from 37.1 kilograms of dried clover flowers.

Isolation of a New Glucoside, Trifolin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}, \text{H}_2\text{O}$.

The original aqueous liquid (A), which had been extracted with ether, as already described, was kept for a considerable time, when it was observed that a quantity (about 60 grams) of a light brown solid had been deposited. This was collected, and purified by repeated crystallisation from aqueous pyridine, when it separated in minute, slender, pale yellow needles, melting and decomposing at about 260° . The substance contained water of crystallisation, which was lost at 115° , but was again absorbed on exposing the anhydrous substance to the air:

0.3051, on heating at 115° , lost $0.0130 \text{ H}_2\text{O}$. $\text{H}_2\text{O}=4.3$.

0.1101 * gave 0.2302 CO_2 and $0.0464 \text{ H}_2\text{O}$. $\text{C}=57.0$; $\text{H}=4.7$.

0.1194 * „ 0.2481 CO_2 „ $0.0506 \text{ H}_2\text{O}$. $\text{C}=56.7$; $\text{H}=4.7$.

0.1010 * „ 0.2115 CO_2 „ $0.0440 \text{ H}_2\text{O}$. $\text{C}=57.1$; $\text{H}=4.8$.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=3.7$ per cent.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}$ requires $\text{C}=57.1$; $\text{H}=4.8$ per cent.

These results indicated the formula of the above-described substance to be $\text{C}_{22}\text{H}_{22}\text{O}_{11}$, and it proved to be a glucoside. As it is a new compound, it is proposed to designate it *trifolin*, with reference to the generic name of the plant from which it was obtained.

Trifolin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}, \text{H}_2\text{O}$, is insoluble in chloroform, benzene, or cold water. It is not readily dissolved by alcohol, but is very soluble in pyridine, and is best crystallised from a mixture of the latter solvent with water. With aqueous sodium carbonate and the alkali hydroxides, it gives intensely yellow solutions. It dissolves in concentrated sulphuric acid, forming at first a yellow solution, but which rapidly develops a brilliant green fluorescence. In alcoholic solution it gives with ferric chloride a dark brown coloration. No crystalline acetyl derivative of trifolin could be prepared.

* Anhydrous substance.

Hydrolysis of Trifolin: Formation of a Yellow Colouring Matter, Trifolitins, $C_{16}H_{10}O_6$.

Trifolin was dissolved in alcohol, a little dilute sulphuric acid added, and the mixture heated on the water-bath for an hour. The alcohol was then removed by distillation in a current of steam, when a yellow, crystalline substance separated. This was collected, and washed with cold water, the filtrate having been set aside for the subsequent examination of the sugar. Some difficulty was experienced in satisfactorily crystallising the yellow hydrolytic product, for it is extremely soluble in alcohol, and invariably separates from dilute alcohol at the ordinary temperature in an apparently amorphous condition. On the other hand, if the alcohol is removed from the solution at the boiling temperature, the substance then separates from the hot liquid in thin, yellow needles. It is, however, best purified by crystallisation from moist nitrobenzene, when it separates in clusters of slender, yellow needles, which melt and decompose at about 275° . After drying at 130° , it was analysed:

0.0786 gave 0.1846 CO_2 and 0.0264 H_2O . $C=64.1$; $H=3.7$.

$C_{16}H_{10}O_6$ requires $C=64.4$; $H=3.4$ per cent.

By heating the yellow hydrolytic product with acetic anhydride an *acetyl* derivative was obtained. The latter, when crystallised from alcohol, separated in colourless, silky needles, which, when rapidly heated, melted at about 116° , then resolidified, and finally melted at 182° . This behaviour was due to the presence of water of crystallisation, the melting point of the anhydrous substance being 182° :

0.5676, on heating at 105° , lost 0.0231 H_2O . $H_2O=4.1$.

$C_{16}H_6O_6(CO \cdot CH_3)_4, H_2O$ requires $H_2O=3.7$ per cent.

The anhydrous substance was analysed, and its molecular weight determined, with the following results:

0.1078 gave 0.2426 CO_2 and 0.0401 H_2O . $C=61.4$; $H=4.1$.

0.1056 „ 0.2375 CO_2 „ 0.0391 H_2O . $C=61.3$; $H=4.1$.

0.4012, in 28.14 of phenol, gave $\Delta t = 0.216^{\circ}$. M.W. = 495.

$C_{16}H_6O_6(CO \cdot CH_3)_4$ requires $C=61.8$; $H=3.9$ per cent. M.W. = 466.

In order to ascertain the number of acetyl groups in the above compound, it was dissolved in alcohol, dilute sulphuric acid added, and the mixture heated for several hours on the water-bath. The alcohol was then completely removed by distillation in a current of steam, and, after cooling, the precipitated yellow substance was collected and weighed, it having been found that the amount dissolved by the water was negligible:

0.1811 gave 0.1160 of colouring matter, or 64.1 per cent.

0.2922 „ 0.1876 „ „ 64.2 „

$C_{16}H_6O_6(CO \cdot CH_3)_4$ requires $C_{16}H_{10}O_6 = 63.9$ per cent.

The yellow colouring matter, as obtained from the above-described acetyl derivative, was crystallised from dilute alcohol, dried at 120° , and again analysed:

0.0855 gave 0.2000 CO_2 and 0.0276 H_2O . $C = 63.8$; $H = 3.6$.

$C_{16}H_{10}O_6$ requires $C = 64.4$; $H = 3.4$ per cent.

It is evident from the above results that the yellow colouring matter obtained by the hydrolysis of the glucoside trifolin possesses the formula $C_{16}H_{10}O_6$, and that it contains four hydroxyl groups. As no compound of this formula, having the same properties, has hitherto been recorded, it is proposed to designate it *trifolitin*.

Trifolitin, $C_{16}H_{10}O_6$, is readily soluble in alcohol and glacial acetic acid, but only very sparingly soluble in benzene, chloroform, or ether. It dissolves in alkalis with an intense yellow colour, and dyes mordanted cotton wool a bright yellow. When dissolved in concentrated sulphuric acid, it gives a yellow solution, followed by a brilliant green fluorescence. It is precipitated from its alcoholic solution by basic lead acetate as an orange-yellow lead salt. In alcoholic solution it gives with ferric chloride a dark green coloration. Trifolitin is not altered when heated for several hours with 30 per cent. aqueous potassium hydroxide, and it contains no methoxyl group. It is evident from its empirical formula, $C_{16}H_{10}O_6$, that it cannot belong to the flavone group of natural colouring matters, and it differs, moreover, from the flavone compounds by the fact that it forms no salt with sulphuric acid (Trans., 1896, 80, 206), whilst it is only with difficulty that a potassium salt is deposited from its concentrated alcoholic solution on the addition of potassium acetate. On the other hand, the composition and general properties of trifolitin would agree with those of a tetrahydroxy-derivative of phenylnaphthaquinone, but the amount of material available was not sufficient to enable us definitely to ascertain the group of naturally occurring dyes to which it belongs.

The aqueous liquid obtained in the course of hydrolysis of the glucoside trifolin was treated with barium carbonate for the removal of the sulphuric acid, and evaporated to the consistency of a syrup. This liquid readily reduced Fehling's solution, and yielded a crystalline osazone which, in the crude condition, melted and decomposed at 180° . When crystallised from aqueous pyridine, it separated in needles, which melted and decomposed at 194° :

0.1258 gave 0.2902 CO_2 and 0.0738 H_2O . $C = 62.9$; $H = 6.5$.

$C_{18}H_{22}O_3N_4$ requires $C = 63.2$; $H = 6.4$ per cent.

The above result indicated that the sugar formed by the

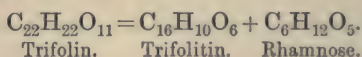
hydrolysis of trifolin has the formula $C_6H_{12}O_5$, and it appeared to be rhamnose, the osazone of which, however, is stated to melt at 180° . For the purpose of comparison, an osazone was prepared from a commercial specimen of rhamnose. This, when crystallised from aqueous pyridine, was found to melt and decompose at 188° , and appeared to be identical with that above described. Trifolin is therefore converted by hydrolysis into trifolitin and rhamnose. A known weight of the glucoside was subsequently hydrolysed by dilute sulphuric acid in aqueous alcohol, the alcohol then removed by passing steam through the mixture, and, after cooling, the precipitated trifolitin was collected, washed with cold water, dried at 120° , and weighed:

0.2056 gave 0.1318 of hydrolytic product, or 64.1 per cent.

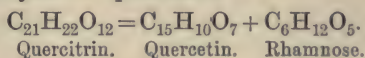
0.2885 „ 0.1859 „ „ 64.4 „

$C_{22}H_{22}O_{11}$ requires $C_{16}H_{10}O_6 = 64.5$ per cent.

The hydrolysis of trifolin therefore takes place according to the following equation:



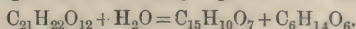
This equation would appear to indicate that the formation of trifolitin and rhamnose from trifolin is unaccompanied by the absorption of water, and would thus be analogous to that representing the hydrolysis of quercitrin*:



The explanation of this apparent anomaly may be, either that these glucosides tenaciously retain a molecule of water, or that the respective phenolic hydrolytic products suffer dehydration immediately after their formation.

The dark-coloured aqueous liquid from which the above-described glucoside, trifolin, had separated was next shaken repeatedly with hot amyl alcohol. The amyl alcohol extracts were united, washed with a little water, and then concentrated under diminished pressure, when, on cooling, a yellow, gelatinous substance was deposited. This was removed by filtration, and the filtrate again concentrated, when a further quantity of a yellow substance was obtained. To the final amyl-alcoholic filtrate, light petroleum was added, which

* The hydrolysis of quercitrin is usually represented as follows :



This equation, however, is evidently incorrect, inasmuch as it is now known that rhamnose possesses the formula $C_6H_{12}O_5$, but crystallises with one molecule of water (compare A. G. Perkin, *J. Soc. Chem. Ind.*, 1903, **22**, 602, and Brauns, *Arch. Pharm.*, 1904, **242**, 561).

precipitated the remainder of the yellow substance as an amorphous powder. The three fractions thus obtained were separately examined.

Fraction I.—This product consisted of a yellow, highly hygroscopic substance. It was dissolved in hot alcohol, and the solution kept for some time, when a gelatinous, brown mass separated. The latter was twice subjected to the preceding treatment with alcohol, when a crystalline substance was obtained, which was finally purified by crystallisation from dilute alcohol. It then formed colourless, glistening leaflets, melting at 214° . The amount of pure substance isolated was 0.5 gram:

0.0989 gave 0.2199 CO_2 and 0.0440 H_2O . $\text{C} = 60.6$; $\text{H} = 4.9$.

0.1154 „ 0.2559 CO_2 „ 0.0496 H_2O . $\text{C} = 60.5$; $\text{H} = 4.8$.

$\text{C}_{14}\text{H}_{12}\text{O}_6$ requires $\text{C} = 60.9$; $\text{H} = 4.3$ per cent.

This substance would thus appear to possess the formula $\text{C}_{14}\text{H}_{12}\text{O}_6$, and, as it differs in its properties from any substance of this formula which has hitherto been recorded, it may be regarded as a new compound.

The compound, $\text{C}_{14}\text{H}_{12}\text{O}_6$, is insoluble in water, chloroform, or benzene, but readily soluble in hot alcohol. It is insoluble in aqueous sodium carbonate, but readily dissolves in alkali hydroxides without change of colour. It gives no coloration with concentrated sulphuric acid, and is not changed by heating with dilute sulphuric acid. Its alcoholic solution yields with ferric chloride a light green coloration.

Isolation of a Second Glucoside of Trifolitin, isoTrifolin, $\text{C}_{22}\text{H}_{22}\text{O}_{11}$.

Fraction II.—This product, consisting of a light yellow powder, was fractionally crystallised from alcohol. The more soluble portion contained a substance which separated from very dilute alcohol in pale yellow needles, melting and decomposing at about 250° with the formation of a deep red liquid. It was dried at 115° :

0.1100 gave 0.2282 CO_2 and 0.0451 H_2O . $\text{C} = 56.6$; $\text{H} = 4.6$.

$\text{C}_{22}\text{H}_{22}\text{O}_{11}$ requires $\text{C} = 57.1$; $\text{H} = 4.8$ per cent.

The glucosidic character of this substance was proved by heating with dilute sulphuric acid in aqueous alcohol. On removing the alcohol, a yellow colouring matter separated from the hot solution in thin needles, which melted and decomposed at 275° . This hydrolytic product yielded an acetyl derivative, which was found to be identical with that prepared from the previously described trifolitin, $\text{C}_{16}\text{H}_{10}\text{O}_6$. The aqueous liquid obtained in the course of the above hydrolysis readily reduced Fehling's solution, but the amount of glucoside available (0.5 gram) did not permit of preparing an osazone from the sugar.

Although the above-described glucoside yields the same yellow hydrolytic product, and possesses apparently the same empirical formula as the glucoside trifolin, the two compounds are evidently not identical. Thus trifolin (m. p. 260°) separates from dilute alcohol in small, globular aggregates of fine needles, whilst the glucoside, melting at 250° , is much more soluble, and crystallises in clusters of comparatively large needles. It is therefore proposed to designate the second glucoside of trifolitin as *isotrifolin*.

The general behaviour of *isotrifolin*, as might be expected, is very similar to that of trifolin. It dissolves in alkalis with the formation of a deep yellow solution. With concentrated sulphuric acid, a yellow coloration is produced, together with a green fluorescence, and in alcoholic solution it gives with ferric chloride a deep brown colour.

Isolation of a Glucoside of Quercetin.

The sparingly soluble portion of the above-described fraction II was finally purified by crystallisation from water, when it separated in pale yellow, prismatic needles, melting and decomposing at 235° :

0.1484, on heating at 110° , lost 0.0161 H_2O . $\text{H}_2\text{O}=10.8$.

0.1117, dried at 110° , gave 0.2184 CO_2 and 0.0475 H_2O .

$\text{C}=53.3$; $\text{H}=4.7$.

The substance dissolved readily in hot water, giving a yellow solution, the colour of which was greatly intensified by the addition of alkalis. With concentrated sulphuric acid, a green fluorescence was produced. Its aqueous solution gave with ferric chloride a dark green coloration.

On heating the substance for a short time in aqueous solution with dilute sulphuric acid, a crystalline, yellow compound separated, and the filtrate from the latter readily reduced Fehling's solution. It was thus evident that the substance was a glucoside. The yellow hydrolytic product melted and decomposed at 305° , and, by means of its acetyl derivative (m. p. 195°), was identified as quercetin. The amount of this glucoside obtained from 37.1 kilograms of dried red clover flowers was only about 0.5 gram, and it was therefore not possible more definitely to characterise it.

Fraction III.—This was a yellow, amorphous solid, which was freely soluble in alcohol, giving a dark-coloured solution. The attempts to obtain something crystalline from this solution were unsuccessful, and as a preliminary test indicated the presence of glucosidic substances, the whole of the fraction, together with the mother liquors from fractions I and II, was hydrolysed by heating for some time with dilute sulphuric acid in aqueous alcohol. After removing the alcohol, a quantity of a dark-coloured solid separated,

which was collected and washed with water. This product was found to be a highly complex mixture, which, however, by digestion with ether, could be separated into readily and sparingly soluble portions. The ethereal solution of the readily soluble portion was extracted with alkalis, when it yielded traces of salicylic acid, a small amount of pratol, $C_{16}H_{12}O_4$, and a yellow compound melting at 305° , which, by means of its acetyl derivative (m. p. 194°), was identified as quercetin.

Isolation of isoRhamnetin, $C_{16}H_{12}O_7$.

The portion of the above-mentioned hydrolytic product which was sparingly soluble in ether was treated with aqueous sodium carbonate, when it was found to be only partly soluble in the alkaline liquid. From the insoluble portion a small amount of the previously described compound, $C_{14}H_{12}O_6$ (m. p. 214°), was obtained, whilst the portion soluble in the alkali carbonate consisted chiefly of a yellow colouring matter, which was observed to differ from any of the substances already isolated from the clover flowers. This substance was sparingly soluble in acetic acid and alcohol, and was purified by conversion into its acetyl derivative, the latter being then fractionally crystallised from alcohol until constant in melting point. It then separated in thin, hair-like needles, melting at $198-200^\circ$. After being dried at 120° :

0.0927 gave 0.2017 CO_2 and 0.0354 H_2O . $C=59.3$; $H=4.2$.

$C_{16}H_8O_7(CO \cdot CH_3)_4$ requires $C=59.5$; $H=4.1$ per cent.

The number of acetyl groups in this derivative was determined by hydrolysis with dilute sulphuric acid, the hydrolytic product being then collected and weighed:

0.1120 gave 0.0722 of colouring matter, or 64.5 per cent.

0.1126 „ 0.0734 „ „ 65.2 „

$C_{16}H_8O_7(CO \cdot CH_3)_4$ requires $C_{16}H_{12}O_7=65.3$ per cent.

The hydrolytic product, which melted and decomposed at about 295° , was a deep yellow substance, only sparingly soluble in alcohol or acetic acid, and insoluble in chloroform or benzene. It dissolved in alkalis, with the production of a deep yellow colour, and its solution in sulphuric acid possessed a green fluorescence. It was found to contain one methoxyl group, as determined by Perkin's modification of the Zeisel method:

0.0941 of acetyl compound gave 0.0379 AgI. $MeO=5.3$.

$C_{15}H_5O_6(OCH_3)(CO \cdot CH_3)_4$ requires $MeO=6.4$ per cent.

From these analytical data it may be concluded that the yellow substance has the empirical formula $C_{16}H_{12}O_7$, and that it contains four hydroxyl groups and one methoxyl group. The composition

and characters of this substance are thus in agreement with those of *isorhamnetin*, a colouring matter which was first isolated by A. G. Perkin (Trans., 1896, **69**, 1658) from the petals of the yellow wallflower (*Cheiranthus Cheiri*). The last-mentioned author had, however, recorded the melting point of tetra-acetyl*isorhamnetin* as 195—196°.

In order to further confirm the identity of the substance contained in red clover flowers with *isorhamnetin*, the product resulting from the methoxyl determination was examined. This separated from the acid solution, on cooling, in yellow, silky needles, which did not melt, but partially volatilised, at a temperature below 300°. It gave an acetyl derivative melting at 190—192°, and possessed the general characters of quercetin, thus affording conclusive evidence that the respective substance in red clover flowers was a monomethyl derivative of quercetin and identical with *isorhamnetin*.

The aqueous liquid which had been extracted with hot amyl alcohol, as above described, was dark brown in colour, and gave an abundant yellow precipitate on the addition of basic lead acetate. This precipitate was examined in the usual way, but, with the exception of a small amount of yellow colouring matter, nothing definite could be isolated from it. The filtrate from the basic lead acetate precipitate, after removal of the excess of lead, was of a bright yellow colour, and readily reduced Fehling's solution. It contained a large quantity of sugar, which yielded *d*-phenylglucosazone, melting at 205°. The liquid was concentrated under diminished pressure to the consistency of a syrup, and kept for a considerable time, but nothing crystalline separated from it.

The Resins (B).

The resinous material obtained from 1·5 kilograms of the original alcoholic extract of red clover flowers was a dark green, soft solid, and amounted to 314 grams. It was dissolved in alcohol, the solution mixed with purified sawdust, and the thoroughly dried mixture then successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained :

Petroleum (b. p. 30—45°) extracted	190·0	grams =	60·5	per cent.
Ether	19·0	„ =	6·1	„
Chloroform	6·7	„ =	2·1	„
Ethyl Acetate	10·3	„ =	3·3	„
Alcohol	43·0	„ =	13·7	„

Total 269·0 grams = 85·7 per cent.

Petroleum Extract of the Resin.

This extract consisted of a dark green, semi-solid fat. It was hydrolysed by heating for a short time with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline mixture repeatedly extracted with ether. The ethereal extracts were united, washed, dried, and the solvent removed, when a quantity (46.5 grams) of a brownish-yellow solid was obtained.

Isolation of Myricyl Alcohol, $C_{31}H_{63}\cdot OH$.

The above-mentioned, brownish-yellow, unsaponifiable material was agitated with cold alcohol, and thus separated into a soluble and an insoluble portion. The latter consisted of a colourless, wax-like solid, melting somewhat indefinitely at 70—74°. It appeared to consist of a mixture of several substances, and was therefore subjected to prolonged fractional crystallisation from a mixture of ethyl acetate and alcohol. In this manner the least soluble constituent was ultimately obtained pure, and then melted at 85°. It crystallised from ethyl acetate in small, colourless needles, whilst from alcohol it separated in glistening leaflets:

0.1250 gave 0.3776 CO_2 and 0.1597 H_2O . $C=82.4$; $H=14.2$.

$C_{31}H_{64}$ requires $C=82.3$; $H=14.2$ per cent.

The analysis and properties of this substance establish its identity as myricyl alcohol.

Isolation of Heptacosane, $C_{27}H_{56}$, Hentriacontane, $C_{31}H_{64}$, and Sitosterol, $C_{27}H_{46}O$.

The more soluble substances obtained in the course of the above fractionation could not be further separated by crystallisation. A preliminary examination having indicated that they consisted chiefly of hydrocarbons, with presumably a little myricyl alcohol, the mixture was heated at 130° for an hour with an equal weight of phthalic anhydride, in order to convert the myricyl alcohol into its acid phthalic ester, and thus effect its removal. The product was subsequently digested with a mixture of ether and chloroform, the solution filtered, and shaken with aqueous sodium carbonate. An insoluble compound thus separated, which was collected, and found to consist of myricyl sodium phthalate. The ether-chloroform solution was then evaporated, and the residue heated with aqueous sodium hydroxide in order to remove unchanged phthalic anhydride. The portion insoluble in the alkali was afterwards dissolved in chloroform, the solution being washed, dried, and the solvent

removed. A wax-like solid was thus obtained, which was subjected to fractional crystallisation from ethyl acetate. The most sparingly soluble fraction, which separated in pearly leaflets, melted at 65° , and this melting point was not changed by further crystallisation:

0.1001 gave 0.3121 CO_2 and 0.1324 H_2O . $\text{C}=85.0$; $\text{H}=14.7$.

$\text{C}_{31}\text{H}_{64}$ requires $\text{C}=85.3$; $\text{H}=14.7$ per cent.

This substance was evidently hentriacontane (m. p. 68°), the somewhat low melting point being probably due to the presence of a small amount of the following hydrocarbon.

From the more readily soluble fractions, a substance was isolated, which separated in pearly leaflets, melting at $58-59^{\circ}$:

0.0944 gave 0.2943 CO_2 and 0.1229 H_2O . $\text{C}=85.0$; $\text{H}=14.5$.

$\text{C}_{27}\text{H}_{56}$ requires $\text{C}=85.3$; $\text{H}=14.7$ per cent.

This substance was thus identified as heptacosane.

The portion of the unsaponifiable material which was soluble in cold alcohol amounted to 30.2 grams. It was twice distilled under diminished pressure, and the following five fractions collected: $200-210^{\circ}$; $210-220^{\circ}$; $220-290^{\circ}$; $290-300^{\circ}$; and above $300^{\circ}/20$ mm.

Fraction $200-210^{\circ}/20$ mm.—This was a pale yellow liquid, and contained a considerable quantity of an unsaturated substance:

0.1083 gave 0.3256 CO_2 and 0.1289 H_2O . $\text{C}=82.0$; $\text{H}=13.2$.

0.1234 absorbed 0.1008 iodine. Iodine value = 81.7.

Fraction $210-220^{\circ}/20$ mm.—This was a brownish-yellow liquid, and, like the preceding fraction, was unsaturated:

0.1064 gave 0.3141 CO_2 and 0.1288 H_2O . $\text{C}=80.5$; $\text{H}=13.5$.

0.0990 absorbed 0.0832 iodine. Iodine value = 84.0.

Both the above fractions were evidently mixtures, and nothing of a definite nature could be obtained from them.

Fractions $220-290^{\circ}$; $290-300^{\circ}$; and above $300^{\circ}/20$ mm.—These fractions solidified on cooling, and were found to consist chiefly of a phytosterol, with a small quantity of the previously mentioned hydrocarbons. After repeated crystallisation, a substance was isolated which separated from a mixture of ethyl acetate and alcohol in colourless, glistening leaflets, melting at $135-136^{\circ}$:

0.3194, on heating at 110° , lost 0.0160 H_2O . $\text{H}_2\text{O}=5.0$.

$\text{C}_{27}\text{H}_{46}\text{O}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=4.5$ per cent.

0.0963, dried at 110° , gave 0.2959 CO_2 and 0.1033 H_2O .

$\text{C}=83.8$; $\text{H}=11.9$.

$\text{C}_{27}\text{H}_{46}\text{O}$ requires $\text{C}=83.9$; $\text{H}=11.9$ per cent.

0.2244 of anhydrous substance, made up to 25 c.c. with chloroform, gave $\alpha_D - 0^{\circ}37'$ in a 2 dm. tube, whence $[\alpha]_D - 34.4^{\circ}$.

The above-described substance was evidently a phytosterol, and it gave the colour reactions of this class of compounds. It yielded an acetyl derivative, melting at 126° , and therefore is identical with sitosterol (*Monatsh.*, 1897, **18**, 551).

Isolation of a New Dihydric Alcohol, Trifolianol, $C_{21}H_{34}O_2(OH)_2$.

The aqueous alkaline solution of potassium salts resulting from the hydrolysis of the petroleum extract of the resin, having been shaken with ether to remove unsaponifiable material, as already described, was acidified with dilute sulphuric acid, when a dark-coloured semi-solid precipitate of fatty acids was produced. On extracting the mixture with ether, however, it was observed that a portion of the precipitate was very sparingly soluble in that liquid. The sparingly soluble material was therefore collected, when it formed a pale green solid, amounting to 3 grams. It was purified by crystallisation from pyridine containing a little alcohol, from which it was deposited in minute, colourless needles, melting and decomposing at 295° . After being dried at 110° :

0.1049 gave 0.2746 CO_2 and 0.0982 H_2O . $C=71.4$; $H=10.4$.

$C_{21}H_{36}O_4$ requires $C=71.6$; $H=10.2$ per cent.

This compound yielded an *acetyl* derivative, which separated from alcohol in flat, colourless needles, melting at $165-166^{\circ}$. An analysis and the determination of its optical rotatory power gave the following results:

0.0968 gave 0.2442 CO_2 and 0.0799 H_2O . $C=68.8$; $H=9.2$.

$C_{21}H_{34}O_4(CO \cdot CH_3)_2$ requires $C=68.8$; $H=9.2$ per cent.

0.2435, made up to 25 c.c. with chloroform, gave $\alpha_D -0^{\circ}30'$ in a 2-dcm. tube, whence $[\alpha]_D -25.7^{\circ}$.

From the above results it was evident that the compound melting at 295° is a dihydric alcohol, having the empirical formula $C_{21}H_{36}O_4$. As it is a new substance, it is proposed to designate it *trifolianol*, with reference to the generic name of the plant from which it was obtained.

Trifolianol, $C_{21}H_{34}O_2(OH)_2$, is practically insoluble in water, and very sparingly soluble in alcohol, ether, and chloroform, but readily soluble in dilute pyridine, from which it crystallises in minute needles. When dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, it gives a transient pink coloration, changing to blue, and finally to green. The properties of trifolianol are similar to those of two other dihydric alcohols which have recently been isolated in these laboratories, namely, ipuranol, $C_{23}H_{38}O_2(OH)_2$ (*Amer. J. Pharm.*, 1908, **80**, 264, 576; *Trans.*, 1908, **93**, 907; 1909, **95**, 249),

and citrullol, $C_{22}H_{36}O_2(OH)_2$ (this vol., p. 102). These alcohols therefore appear to be members of a homologous series, which is represented by the general formula, $C_nH_{2n-6}O_4$.

Examination of the Fatty Acids.

The ethereal solution, from which the above-described trifolianol had been removed by filtration, was washed, dried, and the solvent removed. The mixture of fatty acids thus obtained contained a considerable quantity of resinous material, which was insoluble in light petroleum, and was therefore removed by digesting the mixture with the latter solvent, and filtering. This resin was a dark green solid, amounting to 10 grams, but no definite crystalline compound could be isolated from it. The petroleum solution, on evaporation, yielded a dark-coloured mixture of fatty acids, which was distilled under diminished pressure. The pale yellow distillate, amounting to 60 grams, became partly solid on cooling. It was dissolved in alcohol, when a substance separated which, after several crystallisations from alcohol, melted at 60—61°:

0.1182 gave 0.3236 CO_2 and 0.1341 H_2O . $C=74.7$; $H=12.6$.

0.1280 required for neutralisation 5.02 c.c. $N/10$ -KOH.

Neutralisation value=220.

$C_{16}H_{32}O_2$ requires $C=75.0$; $H=12.5$ per cent.

Neutralisation value=219.1.

This substance was thus identified as palmitic acid.

In order to ascertain the nature of the remaining constituents of the mixed fatty acids, the mother liquors from the above crystallisations were united, and, while hot, fractionally precipitated with a concentrated aqueous solution of barium acetate. The final precipitate was oily, and, as it consisted for the most part of the barium salts of unsaturated acids, it was separately examined as described below. From the other fractions of barium salt the fatty acids were regenerated, and, after one crystallisation from acetic acid, were titrated with a decinormal solution of potassium hydroxide. The neutralisation values of the several fractions were 199.0; 210.0; 213.0; 213.5; 214.8; and 216.9, whilst their melting points were 53—55°; 53—56°; 53—56°; 53—56°; 54—56°; and 56—59° respectively. These results indicated that the saturated acids consisted chiefly of a mixture of palmitic and stearic acids, the respective neutralisation values of which are 219.1 and 197.7.

The acids obtained from the above-mentioned oily barium salt were converted into their lead salts, and the latter treated with ether. From the portion of lead salt which was undissolved by the ether, a further small amount of palmitic acid was obtained. The acids regenerated from the soluble lead salt formed a pale

yellow oil, which was distilled under diminished pressure. An analysis and the determination of its constants gave the following results:

0.1428 gave 0.4031 CO_2 and 0.1437 H_2O . $\text{C}=77.0$; $\text{H}=11.2$.

$d_{20^\circ/20^\circ}=0.9148$. Neutralisation value 200.9. Iodine value 184.7.

$\text{C}_{18}\text{H}_{34}\text{O}_2$ requires $\text{C}=76.6$; $\text{H}=12.1$ per cent. Neutralisation value=198.9. Iodine value=90.1.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ requires $\text{C}=77.1$; $\text{H}=11.4$ per cent. Neutralisation value=200.4. Iodine value =181.4.

$\text{C}_{18}\text{H}_{30}\text{O}_2$ requires $\text{C}=77.7$; $\text{H}=10.8$ per cent. Neutralisation value=201.8. Iodine value=274.0.

In order to ascertain more definitely the nature of the unsaturated acids, 10 grams of the mixture were dissolved in alkali, and oxidised with a 1.5 per cent. solution of potassium permanganate. The chief product of the oxidation, when crystallised from water, separated in thin needles, melting at $156-157^\circ$:

0.0630 gave 0.1426 CO_2 and 0.0594 H_2O . $\text{C}=61.7$; $\text{H}=10.5$.

$\text{C}_{18}\text{H}_{36}\text{O}_6$ requires $\text{C}=62.1$; $\text{H}=10.3$ per cent.

This substance was evidently tetrahydroxystearic acid (sativic acid). In addition to the latter acid, very small quantities of dihydroxystearic acid (m. p. 130°), linusic acid (m. p. $200-205^\circ$), and isolinusic acid (m. p. $173-174^\circ$) were obtained.

The above results would therefore indicate that the unsaturated acids consisted chiefly of linolic acid, with smaller amounts of oleic, linolenic, and isolinolenic acids.

Ethereal Extract of the Resin.

This extract was a black, brittle solid, and amounted to 19 grams. It was digested with 500 c.c. of ether, when the greater portion passed into solution, while a small amount of a light green powder remained undissolved. The latter was collected, and boiled with alcohol, in which it was very sparingly soluble, in order to remove the green colouring matter. It was finally crystallised from a mixture of pyridine and alcohol, when it separated in colourless needles, melting and decomposing at about 290° . It yielded an acetyl derivative, melting at 166° , which was analysed:

0.0854 gave 0.2142 CO_2 and 0.0690 H_2O . $\text{C}=68.4$; $\text{H}=9.0$.

$\text{C}_{21}\text{H}_{34}\text{O}_4(\text{CO}\cdot\text{CH}_3)_2$ requires $\text{C}=68.8$; $\text{H}=9.2$ per cent.

The above-described substance, when dissolved in chloroform with a little acetic anhydride, and a drop of concentrated sulphuric acid subsequently added, gave a pink coloration, rapidly changing to blue, and finally to green. It was evidently identical with the

dihydric alcohol designated as trifolianol, which had previously been isolated from the petroleum extract of the resin.

The above-mentioned ethereal solution of the ethereal extract was shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide, and the various extracts thus obtained were separately examined. The ammonium carbonate removed only traces of a green resin. The first sodium carbonate extract yielded, on acidification, a dark green resin, which consisted chiefly of chlorophyll, whilst the subsequent sodium carbonate extract, when acidified, gave a nearly colourless precipitate. This was collected and dissolved in alcohol, when a small amount of a substance separated in colourless, talon-like needles, melting at 253° . This substance was found to be identical with the compound designated as pratol, $C_{16}H_{12}O_4$, which had previously been isolated from the portion of the alcoholic extract of clover flowers which was soluble in water. The mother liquors from the crystallisation of the pratol deposited a little of a crystalline substance, melting somewhat indefinitely between 178° and 183° , but the amount was too small to permit of its further examination. The final extraction of the ethereal liquid with sodium hydroxide yielded nothing but amorphous products, and on subsequently evaporating the ether only traces of a soft resin remained.

Chloroform and Ethyl Acetate Extracts of the Resin.

These extracts were black, brittle solids. They were small in amount, and nothing crystalline could be isolated from them.

Alcohol Extract of the Resin.

This was a dark brown, brittle solid, amounting to 43 grams. In order to ascertain whether it contained anything glucosidic, it was heated for some time with a 5 per cent. solution of sulphuric acid in aqueous alcohol, and the mixture subsequently distilled with steam, but no volatile oil or acid passed over. The distillation flask then contained, besides the aqueous liquid, a quantity of a black resin, which was collected and examined, but nothing definite could be isolated from it. The aqueous liquid, on the other hand, when extracted with ether, yielded a small quantity of a viscid, yellow oil, which gradually deposited a solid substance. The latter was crystallised from alcohol, when it separated in colourless needles, melting at 250° , and gave an acetyl derivative melting at 166° . It proved to be identical with the previously described substance, $C_{16}H_{12}O_4$, designated as pratol. The aqueous liquid,

which had been extracted with ether as above described, was freed from sulphuric acid by means of baryta, and concentrated to a small volume. It then readily reduced Fehling's solution, and yielded a small quantity of an osazone, melting at 203° . These facts indicated the presence of a glucoside in the alcoholic extract of the resin, and it is probable that the small amount of pratol, $C_{16}H_{12}O_4$, obtained from the latter represents one of its hydrolytic products.

Summary.

The detailed results of the present investigation of red clover flowers (*Trifolium pratense*, Linné) may be summarised as follows:

A quantity of the alcoholic extract, representing 37.1 kilograms of the dried flowers, when distilled with steam, yielded 10.5 grams, or 0.028 per cent., of essential oil. This essential oil, which contained furfuraldehyde, possessed the following constants: $d_{20^{\circ}}/20^{\circ} = 0.9476$; $\alpha_D + 4.0'$ in a 1-dcm. tube.

The portion of the alcoholic extract which was soluble in water contained a large amount of sugar, which yielded *d*-phenylglucosazone (m. p. 205°), but from the aqueous liquid the following definite substances were isolated: salicylic and *p*-coumaric acids; isorhamnetin, $C_{16}H_{12}O_7$ (m. p. 295°), which was probably present in the form of a glucoside; a number of new phenolic substances: pratol, $C_{15}H_8O_2(OH)(OCH_3)$, m. p. 253° , which apparently is a hydroxymethoxyflavone, and yields an *acetyl* derivative melting at 166° ; pratensol, $C_{17}H_9O_2(OH)_3$, m. p. 210° , which yields a *triacetyl* derivative melting at 189° ; a yellow compound, $C_{16}H_{10}O_7$ (m. p. 280°), which yields a *tetra-acetyl* derivative melting at 145 – 147° ; a substance, $C_{15}H_7O_3(OH)_3$, m. p. 225° , which yields a *triacetyl* derivative melting at 209° ; a substance, $C_{14}H_{12}O_6$ (m. p. 214°); also the following new glucosides: trifolin, $C_{22}H_{22}O_{11} \cdot H_2O$ (m. p. 260°), which yields on hydrolysis a yellow colouring matter, trifolitin, $C_{16}H_{10}O_6$ (m. p. 275°), and rhamnose, $C_6H_{12}O_5$; iso-trifolin, $C_{22}H_{22}O_{11}$ (m. p. 250°), and a glucoside of quercetin, melting at 235° .

The portion of the alcoholic extract which was insoluble in water consisted chiefly of resinous material, the amount of which was equivalent to 5.6 per cent. of the weight of dried clover flowers. From the resin the following compounds were obtained: myricyl alcohol, $C_{31}H_{63} \cdot OH$; heptacosane, $C_{27}H_{56}$, and hentriacontane, $C_{31}H_{64}$; sitosterol, $C_{27}H_{46}O$ (m. p. 135 – 136° ; $[\alpha]_D - 34.4^{\circ}$); a new dihydric alcohol, trifolianol, $C_{21}H_{34}O_2(OH)_2$ (m. p. 295°), which appears to be a homologue of ipuranol, $C_{23}H_{38}O_2(OH)_2$, and yields a *diacetyl* derivative melting at 165 – 166° and having $[\alpha]_D - 25.7^{\circ}$; a mixture of fatty acids, consisting chiefly of palmitic, stearic, and

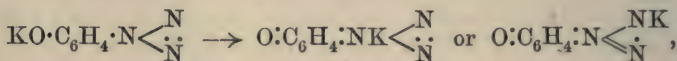
linolic acids, with small amounts of oleic, linolenic, and *isolinolenic* acids. A small amount of pratol, $C_{16}H_{12}O_4$, was likewise obtained, the latter having evidently been present in the resin in the form of a glucoside.

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XXVII.—*The Triazo-group. Part XII. Derivatives of para-Triazobenzaldehyde.*

By MARTIN ONSLOW FORSTER and HILDA MARY JUDD.

AN investigation of the hydroxyphenylazoimides (Trans., 1907, 91, 855 and 1350) brought to light a characteristic distinction between the potassium derivative of the para-compound and those of the ortho- and meta-triazophenols depending on the change of colour which takes place when the solution in water or absolute alcohol is heated; as a consequence of this treatment, the colourless substance is transformed into a dark blue material, which appears to be isomeric with its generator. The explanation of this behaviour which suggested itself at the time depends on the possibility of rearrangement having taken place in accordance with the following formulæ:



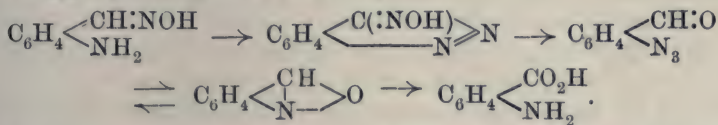
and although it was not possible to recognise any substantial difference between the acyl derivatives prepared from the blue compound and those obtained from the colourless potassium salt, they were certainly more highly coloured; moreover, whilst the *p*-triazophenol liberated from it by acids appears to have the general properties of the original material, the solid potassium derivative regenerated by the action of alkali is not colourless, but bluish-green.

The absence of any similiar colour change in the case of ortho- and meta-hydroxyphenylazoimides has led us to examine certain para-derivatives of triazobenzene in which the occurrence of hydrogen in the group occupying the para-position afforded an opportunity of rearrangement on the lines indicated above. The condensation products from *p*-triazobenzaldehyde with hydroxylamine, phenylhydrazine, and *p*-aminophenol might have been expected, under favourable circumstances, to yield coloured modifications depending on transposition of hydrogen:

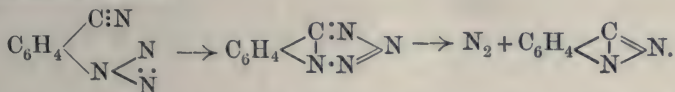


In no case, however, has any indication of a colour change by alkali been observed, and although it certainly happens that a chloroform solution of *p*-triazobenzaldehydephenylhydrazone rapidly becomes brown and ultimately purple when exposed to light, the observations of Chattaway (*Trans.*, 1906, **89**, 462) in connexion with the alteration which benzaldehydephenylhydrazone undergoes, would suggest correspondence between the two phenomena.

There does not appear to be any tendency on the part of the triazo-group in *p*-triazobenzaldehyde to enter into association with the aldehyde radicle in the manner brought to light by Bamberger and Demuth (*Ber.*, 1901, **34**, 1309) during an investigation of certain ortho-aminobenzaldoximes. These authors found that on diazotising *o*-aminobenzaldoxime there is produced indiazoneoxime, isomeric with *o*-triazobenzaldehyde, into which it passes on treatment with alkali or warm water; furthermore, they showed that *o*-triazobenzaldehyde may be converted readily into anthranilic acid through anthranil, from which they regenerated it by the combined action of hydroxylamine and oxygen (*loc. cit.*, 3874 and 4015):



As the production of anthranil from *o*-triazobenzaldehyde must depend on an opening of the azoimide ring analogous to that incurred by diazomethane when this compound transforms aldehydes into ketones (Schlotterbeck, *Ber.*, 1907, **40**, 479; 1909, **42**, 2559), it seemed reasonable to expect a similar transformation in the case of *o*-triazobenzonitrile:



The substance in question was therefore prepared by the action of hydrazoic acid on *o*-cyanobenzenediazonium chloride; it was found that alkali, however, which transforms *o*-triazobenzaldehyde into anthranilic acid with loss of nitrogen, leaves the triazo-group in *o*-triazobenzonitrile intact, the substance being merely hydrolysed to

o-triazobenzoic acid. During this process there does not occur any elimination of the triazo-group in the form of alkali azide, and the same power of resistance is displayed by the triazo-group in *p*-triazobenzaldoxime. These observations are of some interest in connexion with the effect produced by other groups on the tenacity with which the azoimide complex is held by the benzene ring. Noelting, Grandmougin, and Michel (*Ber.*, 1892, **25**, 3328) were the first to show that a nitro-group in the ortho- or para-position unloosed the triazo-group, which remained indifferent to the presence of methyl and the meta-nitro-complex; a similar relationship was found applicable to the naphthalene series (Forster and Fierz, *Trans.*, 1907, **91**, 1942), with the addition that a heteronuclear nitro-group in the 5:1, 8:1, 5:2, and 8:2 positions left the azoimide radicle unaffected by alkali. Furthermore it was shown (*loc. cit.*, 1356) that boiling potassium hydroxide solution eliminates 20 per cent. of hydrazoic acid from *p*-hydroxyphenylazoimide without yielding a trace of this product from the ortho-derivative.

We have taken this opportunity to study the relationship of the oximes obtainable from *p*-triazobenzaldehyde, and find that the production and properties of these substances are governed by the same generalisations which prevail among their better known analogues. The *anti*-aldoxime, melting at 98°, is the direct product of treating the aldehyde with hydroxylamine, and is converted by the action of hydrogen chloride in dry ether into the *syn*-aldoxime, which melts at 142°. The latter modification is labile, being transformed into the more fusible isomeride at 100°, and on treatment with benzoyl chloride in pyridine yields the same benzoyl derivative as that obtained from the *anti*-aldoxime; the *p*-triazobenzaldoximes thus resemble the unsubstituted compounds, from which only one benzoyl derivative is obtainable. On consulting the literature we found that the benzoyl derivative of benz-*anti*-aldoxime was produced by direct action of benzoyl chloride (Minunni and Corselli, *Gazzetta*, 1892, **22**, ii, 167), and consequently in presence of hydrogen chloride. Nevertheless we have failed to obtain an isomeric benzoyl derivative under modified conditions, the only product arising by the action of benzoyl chloride on the dry sodium derivative of both benzaldoximes in ether consisting of the substance melting at 101° described by Minunni and Corselli; benzoylation in dry pyridine or in presence of aqueous alkali was equally unsuccessful. The benzoyl derivative of *p*-triazobenzaldoxime is readily decomposed into *p*-triazobenzonitrile and benzoic acid, and on attempting to prepare the *p*-toluenesulphonyl derivative, this nitrile was the sole recognisable product. From the sodium derivative of benz-*anti*-aldoxime, however, a very unstable *p*-toluenesulphonyl compound has been prepared, melting at 88°, and

undergoing decomposition into benzonitrile at the laboratory temperature; the *syn*-aldoxime did not yield a *p*-toluenesulphonyl derivative, however, even when exactly the same conditions were observed, benzonitrile alone being formed, and it is noteworthy in this connexion that the nitrile was produced from both oximes by the action of benzenesulphonyl chloride in pyridine (Werner and Piguet, *Ber.*, 1904, 37, 4308). β -Naphthalenesulphonyl chloride appears to be incapable of attacking the isomeric benzaldoximes and their *p*-triazoderivatives in pyridine at zero.

EXPERIMENTAL.

The p-Triazobenzaldoximes, N₃·C₆H₄·CH·NOH.

The *p*-triazobenzaldehyde required for the preliminary experiments was prepared by the action of sodium carbonate on a solution of diazotised *p*-aminobenzaldehyde to which hydroxylamine hydrochloride had been added (Rupe and von Majewski, *Ber.*, 1900, 33, 3401), but we subsequently obtained a more satisfactory product by the following process.

Fifty grams of finely powdered *p*-aminobenzaldehyde were mixed with crushed ice, stirred with 150 c.c. of concentrated hydrochloric acid, and diazotised with 25 grams of sodium nitrite in the minimum of water; after half an hour some carbamide was added, and the liquid filtered rapidly from tar. The ice-cold diazonium salt, now clear and orange-yellow, was treated with 20 grams of sodium azide, added gradually in aqueous solution; brisk evolution of nitrogen occurred, and the triazobenzaldehyde separated in the form of a pale brown oil, which, after an hour, was extracted with ether, shaken twice with 10 per cent. hydrochloric acid, and dried with calcium chloride, thereby losing much of the brown impurity. The triazobenzaldehyde weighed 32 grams.

p-Triazobenz-anti-aldoxime was prepared by adding 6 grams of hydroxylamine hydrochloride to 5 grams of the aldehyde suspended in 50 c.c. of 15 per cent. potassium hydroxide, the characteristic odour of *p*-triazobenzaldehyde, which recalls anise, being no longer perceptible after half an hour. Carbon dioxide was then passed through the liquid, and the deep brown precipitate recrystallised from dilute alcohol, forming lustrous plates which melt at 98°:

0.1119 gave 33 c.c. N₂ at 16° and 769 mm. N = 34.80.

C₇H₆ON₄ requires N = 34.56 per cent.

The substance is freely soluble in methyl and ethyl alcohols, ethyl acetate, chloroform, ether, glacial acetic acid, acetone, or carbon tetrachloride; benzene dissolves it less readily, and petroleum

sparingly, depositing it in flat, pale yellow needles. It is volatile in steam, and when crystallised from boiling water is practically colourless. Ether extracts small quantities from solutions in alkali hydroxide. When exposed to light the substance rapidly becomes dark brown, but there is no change of colour when a solution in 50 per cent. potassium hydroxide is boiled, unaltered material being recovered on atidification; moreover, one gram of the substance was heated with 20 per cent. aqueous potassium hydroxide during four hours on the water-bath without yielding a trace of potassium azide. Torrents of gas were liberated by concentrated sulphuric acid, which formed a dark brown liquid indifferent towards Fehling's solution. Stannous chloride in hydrochloric acid also sets free gas, yielding a bright red solution, from which a dark reddish-brown precipitate quickly separated; this material, probably an azo-compound, is insoluble in benzene, but dissolves in alcohol, the deep red solution becoming yellow with alkali and having its red colour restored by acids.

The *methyl ether* was obtained by the silver oxide method as a colourless oil having a powerful odour of anise, and also arises by the action of diazomethane on a solution of the oxime in dry ether (Forster and Dunn, Trans., 1909, 95, 425); it is readily volatile in steam, and is not dissolved by alkalis.

p-Triazobenz-syn-aldoxime arose in the form of hydrochloride on passing dry hydrogen chloride into a solution of the *anti*-oxime (m. p. 98°) in ether. The salt, after being washed with ether, was suspended in this medium and decomposed with sodium carbonate, the ethereal solution of the *syn*-oxime being then dried by sodium sulphate and evaporated at the laboratory temperature. The colourless, crystalline residue was recrystallised from warm benzene, which deposited a felted mass of very pale yellow, silky needles:

0.0498 gave 14.2 c.c. N_2 at 10.5° and 775 mm. $N = 34.64$.

$C_7H_6ON_4$ requires $N = 34.56$ per cent.

The melting point, 142°, is sharp, although the substance decomposes. The oxime is readily soluble in methyl and ethyl alcohols, from which water precipitates lustrous, slender needles; it is freely soluble in cold ethyl acetate, chloroform, ether, acetone, or glacial acetic acid, but is only sparingly so in benzene, and almost insoluble in light petroleum. It resembles the more fusible isomeride in being very sensitive to light, volatile in steam, and extractable by ether from its alkaline solutions. Unlike the *syn*-modification of benzaldoxime and its nitro-derivatives, the triazo-compound appears to resist any tendency to undergo transformation into the *anti*-form on recrystallisation, and must be heated for several minutes at 100° before the

isomeride is regenerated; the *syn*-oxime may even be recovered unchanged from a solution in 10 per cent. potassium hydroxide which has been heated in steam during fifteen minutes.

Action of Acyl Chlorides on the Oximes.—On mixing pyridine solutions containing 1.4 grams of benzoyl chloride and 1.6 grams of the *anti*-aldoxime, the temperature rose, and the liquid was therefore surrounded with melting ice during one hour, and afterwards poured into cold water; the oil precipitated in this manner became semi-solid on treatment with dilute acetic acid, and after being rubbed with a few drops of cold alcohol and drained on earthenware, yielded a colourless solid, only moderately soluble in alcohol, from which it crystallised in minute, lustrous needles melting at 146° with decomposition:

0.1325 gave 23.5 c.c. N_2 at 11° and 758 mm. $N = 21.12$.

$C_{14}H_{10}O_2N_4$ requires $N = 21.05$ per cent.

On proceeding in exactly the same way with the *syn*-aldoxime, the product is identical.

It was noticed that if the oil which is precipitated on pouring the pyridine solution into water is allowed to remain in the liquid without adding acetic acid, the benzoyl derivative disintegrates in the course of a few days, yielding *p*-triazobenzonitrile, a specimen of which, after crystallisation from alcohol, melted at 71° , and was therefore identical with the substance obtained by Rupe and von Majewski (*loc. cit.*, 3406) from *p*-cyanobenzenediazonium perbromide and ammonia.

The action of *p*-toluenesulphonyl chloride in pyridine was also studied, and with this agent both oximes were converted into the nitrile. β -Naphthalenesulphonyl chloride, however, appears to be devoid of action, unchanged material being recovered in each case when the isomeric oximes were treated with this compound in pyridine.

Action of Potassium Cyanide on p-Triazobenzaldehyde.

In preparing *p*-triazobenzaldehyde by the process of Rupe and von Majewski, we were led to suspect the occurrence of a subsidiary action indicated by the comparative indifference of the product towards hydroxylamine and phenylhydrazine. As it seemed possible that a portion of the aldehyde had become converted into bis-*p*-triazobenzoin, we attempted to compare this compound by the action of potassium cyanide, but it was soon evident that this agent, instead of effecting benzoin synthesis, had attacked the triazo-group in the manner described by Wolff and Lindenhayn (*Ber.*, 1904, **37**, 2374), giving rise to the potassium derivative of the corresponding triazen, $O:CH \cdot C_6H_4 \cdot N:N \cdot NK \cdot CN$.

Ten grams of the aldehyde in 20 c.c. of absolute alcohol were heated with 2 grams of potassium cyanide in 10 c.c. of water during half an hour under reflux; the liquid deposited a small quantity of potassium cyanide as it cooled, and when filtered from this was allowed to evaporate spontaneously. Bright yellow crystals were obtained embedded in oil, and on recrystallisation from alcohol formed radial groups of long, pale yellow prisms:

0.0435 gave 0.0179 K_2SO_4 . $K = 18.40$.

$C_8H_5ON_4K$ requires $K = 18.40$ per cent.

The salt has not a definite melting point, decomposing at a high temperature with extensive intumescence; it is readily soluble in water, the yellow colour of the solution being destroyed by hydrochloric acid and restored by alkali.

p-Triazobenzaldehydephenylhydrazone, $N_3 \cdot C_6H_4 \cdot CH:N \cdot NH \cdot C_6H_5$.

On mixing 4 grams of *p*-triazobenzaldehyde with 3 grams of phenylhydrazine, water separated immediately, the liquid became hot, and solidified on cooling; the product was recrystallised from methyl alcohol, followed by petroleum, which deposited minute, straw-coloured needles melting at 190° without evolving gas, although steady effervescence began at 120° :

0.1103 gave 28.2 c.c. N_2 at 17° and 767 mm. $N = 29.95$.

$C_{18}H_{11}N_5$ requires $N = 29.53$ per cent.

The phenylhydrazone is freely soluble in cold acetone, benzene, ethyl acetate, and chloroform, the solution in the last named becoming deep brown and ultimately purple when exposed to light; this colour change has not been observed in the case of any other medium, and recalls the observations of Chattaway in connexion with benzaldehydephenylhydrazone (*loc. cit.*). Concentrated sulphuric acid develops a transient, intense blue coloration, followed immediately by liberation of gas; this was also set free by stannous chloride in hydrochloric acid, which ultimately gives rise to a deep reddish-brown precipitate. There is not any change of colour when the substance is heated with concentrated potash in either alcohol or water.

p-Triazobenzaldehyde-*p*-aminophenol, $N_3 \cdot C_6H_4 \cdot CH:N \cdot C_6H_4 \cdot OH$.

Five grams of *p*-aminophenol hydrochloride in water were mixed with 5 grams of sodium acetate and shaken with 5 grams of *p*-triazobenzaldehyde, when the emulsion was transformed into a paste of crystals; after recrystallisation from benzene, the substance was

obtained in lustrous, golden-brown, six-sided plates, melting at 175° with vigorous intumescence:

0.1378 gave 27.5 c.c. N_2 at 14° and 765.5 mm. $N = 23.64$.

$C_{13}H_{10}ON_4$ requires $N = 23.53$ per cent.

The substance is moderately soluble in boiling methyl alcohol, but only sparingly soluble in boiling benzene, and insoluble in boiling petroleum; acetone and ethyl acetate dissolve it readily when warm, depositing the substance in clear-cut, hexagonal prisms, whilst boiling chloroform dissolves it sparingly. When suspended in water and heated with potassium hydroxide, the deep yellow solution of the potassium derivative quickly deposits lustrous crystals, but the sparingly soluble product undergoes no colour change when heated with concentrated potash, aqueous or alcoholic. The substance is decomposed immediately by concentrated sulphuric acid, liberating gas, which is also set free by stannous chloride in hydrochloric acid, the deep red solution rapidly depositing a dark reddish-brown precipitate.

Condensation of p-Triazobenzaldehyde with Camphoryl- ψ -semicarbazide.

Four grams of camphoryl- ψ -semicarbazide nitrate dissolved in water were warmed with two grams of *p*-triazobenzaldehyde, when the liquid became turbid and colourless needles separated. The highly insoluble product was exhausted with a small quantity of boiling absolute alcohol, and then dissolved in a large proportion of boiling acetone; dilution with water led to the separation of transparent, pale yellow, rectangular prisms, infusible below 250° , although suddenly becoming brown at about 200° :

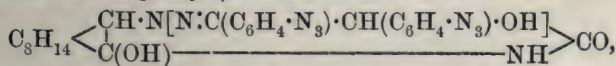
0.1287 gave 0.2948 CO_2 and 0.0587 H_2O . $C = 62.45$; $H = 5.06$.

0.1371 „ 30.8 c.c. N_2 at 15° and 763 mm. $N = 26.46$.

$C_{18}H_{22}O_2N_6$ requires $C = 61.00$; $H = 6.21$; $N = 23.73$ per cent.

$C_{25}H_{25}O_3N_9$ „ $C = 62.11$; $H = 5.17$; $N = 26.09$ „ „

The constitution of the product is somewhat obscure. The analytical results are not in agreement with the empirical formula $C_{18}H_{22}O_2N_6$, that of *p*-triazobenzaldehyde camphoryl- ψ -semicarbazone, and are equally incompatible with the anhydride, which, in view of the readiness with which camphoryl- ψ -semicarbazide loses $1H_2O$, might possibly have arisen. The formula indicated is that of bis-*p*-triazobenzoin camphoryl- ψ -semicarbazone,



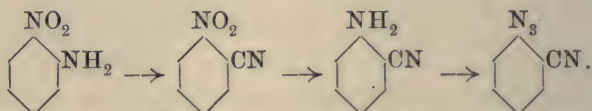
less $1H_2O$, an expression which gains probability from the infusibility of the substance, because the camphoryl- ψ -semicarbazones

already described (*Trans.*, 1905, **87**, 727) melt below 250° , whilst the anhydride of camphoryl- ψ -semicarbazide is not fused until 280° is reached.

A solution containing 0.1745 gram in 25 c.c. of chloroform gave $a_D 7^{\circ}46'$ in a 2-dcm. tube, whence $[\alpha]_D 556.3^{\circ}$, whilst a pyridine solution with 0.2600 gram in 25 c.c. gave $a_D 0^{\circ}30'$ for the same length, corresponding with $[\alpha]_D 24.0^{\circ}$.



The azoimide was produced by the following steps from *o*-nitroaniline:



Adopting the modification of Sandmeyer's method described by Pinnow and Müller (*Ber.*, 1895, **28**, 151), we found that the *o*-nitrobenzonitrile was more conveniently separated from the uninviting product of treatment with cuprous cyanide by allowing the black mass to become dry, extracting it with chloroform, and adding petroleum to the filtered liquid; in this way, 50 grams of *o*-nitroaniline furnished 37 grams of *o*-nitrobenzonitrile in crystalline form. The difficulties which beset the reduction of *o*-nitrobenzonitrile to *o*-aminobenzonitrile have been already described by Pinnow and Müller (*loc. cit.*; compare also Reissert and Grube, *Ber.*, 1909, **42**, 3710), and we isolated the hydrochloride of the base in the manner indicated by them, removing the associated hydrochloride of *o*-aminobenzamide by treatment with cold water.

Fifteen grams of *o*-aminobenzonitrile hydrochloride were suspended in 80 c.c. of hydrochloric acid and diazotised with 25 grams of sodium nitrite; by using a larger proportion of hydrochloric acid than that employed by Pinnow and Samann (*Ber.*, 1896, **29**, 630), the formation of *o*-dicyanodiazaminobenzene, which represented 80 per cent. of the theoretical amount in their experiment, was almost entirely avoided, and the filtered diazonium salt gave *o*-triazobenzonitrile in the form of a colourless precipitate on adding 20 grams of sodium azide. The dried product was recrystallised from petroleum (b. p. $60-80^{\circ}$), which deposits pale yellow, lustrous leaflets, quickly becoming brown when exposed to light; it sinters at 51° , and is completely fused at 58° :

0.0792 gave 27.0 c.c. N_2 at 17° and 748 mm. $N = 38.92$.

$C_7H_4N_4$ requires $N = 38.88$ per cent.

The substance is freely soluble in cold chloroform, ethyl acetate, benzene, or acetone, readily so in alcohol, and more sparingly so in hot petroleum. Although the solid material is odourless, the vapour in steam has a penetrating odour, without suggestion of anise. There is violent decomposition with concentrated sulphuric acid.

Action of Alcoholic Potash.—An alcoholic solution of *o*-triazobenzo-nitrile was heated two hours under reflux with potassium hydroxide dissolved in the minimum quantity of water. Nitrogen was not set free, and on evaporating the solution, potassium azide could not be detected in the residue, which was then dissolved in water and treated with dilute sulphuric acid. The precipitated *o*-triazobenzoic acid was recrystallised from boiling water, from which it separated in minute, lustrous needles, melting and decomposing at 146° ; analysis gave 25.97 per cent. of nitrogen, 25.76 and 34.57 per cent. being required by the formulæ $C_7H_5O_2N_3$ (triazobenzoic acid) and $C_7H_6ON_4$ (triazobenzamide) respectively, and the acid is therefore identical with the one obtained by Griess from anthranilic acid (*Zeitsch. für Chem.*, 1867, 165) and by Bamberger and Demuth (*Ber.*, 1901, 34, 1337) from *o*-triazobenzaldehyde.

Action of Acyl Chlorides on the Isomeric Benzaldoximes.

So far as we have been able to ascertain, the only benzoyl derivative of benzaldoxime is that described by Minunni and Corselli (*loc. cit.*), who prepared it from benz-*anti*-aldoxime and benzoyl chloride in dry ether. In view of the existence of two acetyl derivatives corresponding with the *anti*- and *syn*-aldoximes, it appeared worth while to attempt the production of a benzoyl derivative from benz-*syn*-aldoxime under conditions excluding the presence of free hydrogen chloride.

As a preliminary experiment, the sodium derivative of benz-*anti*-aldoxime suspended in dry ether was treated with the calculated amount of benzoyl chloride, the very vigorous action which ensued being checked by surrounding ice and water; after half an hour, anhydrous sodium carbonate was added to destroy any slight excess of benzoyl chloride, when the filtered solution deposited the known benzoyl derivative melting at 101° . On treating the sodium derivative of benz-*syn*-aldoxime in precisely the same way, the same substance was produced, no depression of melting point occurring on admixture.

An attempt to prepare a *p*-toluenesulphonyl derivative of benz-*anti*-aldoxime by the same process was unsuccessful; the residue left by the solvent remained liquid, and decomposed explosively on slightly raising the temperature, when torrents of gas were liberated, whilst

the tarry residue had the odour of phenylcarbylamine. On shaking the sodium derivative of benz *anti*-aldoxime with *p*-toluenesulphonyl chloride in 5 per cent. sodium hydroxide during two and a-half hours, a strong odour of benzonitrile was developed, and a small proportion of a solid substance remained undissolved; after crystallisation from light petroleum, this melted at 88°, and was prepared more conveniently by rubbing the sodium derivative with *p*-toluenesulphonyl chloride and weak sodium carbonate solution. After remaining twenty-four hours in the ice-chest, the pasty mass, with the odour of phenylcarbylamine, had become brittle, and, when washed with sodium carbonate and dried in the desiccator, was dissolved in cold benzene, from which petroleum precipitated it in lustrous, colourless prisms melting with profound decomposition at 88°:

0.5359 gave 24.6 c.c. N₂ at 24° and 758 mm. N = 5.15.

C₁₄H₁₃O₃NS requires N = 5.09 per cent.

The substance is highly unstable, even when purified, especially if kept in a 'stoppered bottle, undergoing decomposition after forty-eight hours in daylight to a tarry mass which has the odour of benzonitrile; a specimen on a watch-glass in a large desiccator protected from light, however, remained many months without alteration.

On proceeding in the same way with benz *syn*-aldoxime, the only product was benzonitrile, and on substituting β -naphthalenesulphonyl chloride for the toluene derivative, there did not appear to be any action with either oxime.

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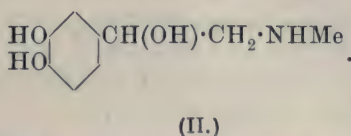
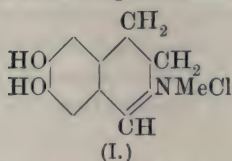
XXVIII.—isoQuinoline Derivatives. Part IV. *ortho*-Dihydroxy-bases. The Conversion of 1-Keto-6:7-dimethoxy-2-alkyltetrahydroisoquinolines into 3:4-Dihydroxyphenylethylalkylamines.

By FRANK LEE PYMAN.

IN the preceding papers of this series (Trans., 1909, 95, 1266, 1610, 1738) a number of 6:7-dimethoxyisoquinoline derivatives have been described. Some of these proved to be physiologically active substances, and it was thought likely that the corresponding 6:7-dihydroxy-bases might be compounds of still more marked physiological action.

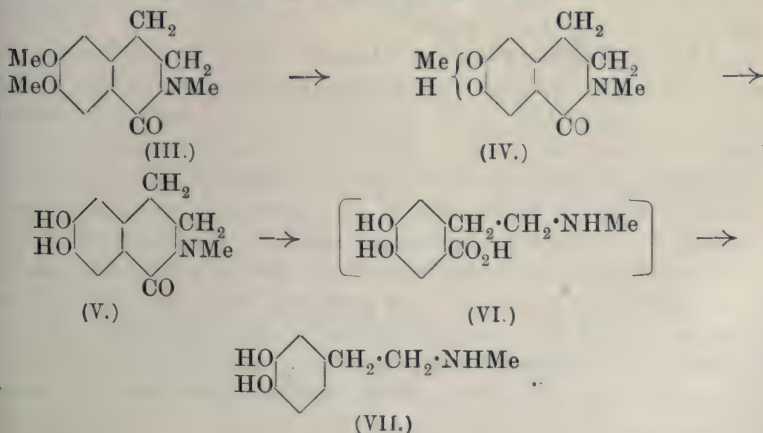
In particular, it seemed possible that compounds of this type, such, for instance, as 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium chloride (I), might produce a pressor effect similar to that caused by

β -3:4-trihydroxyphenylethylmethylamine (II), the *lævo*-modification of which is the active principle of the suprarenal gland, since they would be in some respects similarly constituted:

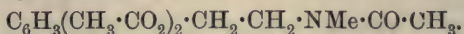


With this object in view, several dimethoxyisoquinoline derivatives have been converted by treatment with hydrochloric acid into the corresponding dihydroxy-bases, which were then submitted to physiological examination, but in no case where the isoquinoline ring remained intact had the resulting dihydroxy-base any marked pressor properties. It was found, however, that the 1-keto-6:7-dimethoxy-2-alkyltetrahydroisoquinolines, when treated with hydrochloric acid at a sufficiently high temperature, gave rise to bases of considerable pressor properties, in which the isoquinoline ring was no longer preserved.

Thus, when 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline (III) is heated with hydrochloric acid under pressure for three hours at 175° , it is quantitatively converted into the hydrochloride of 3:4-dihydroxyphenylethylmethylamine (VII). By working at temperatures lower than 175° , however, two immediate products, 7(or 6)-hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline (IV) and 6:7-dihydroxy-1-keto-2-methyltetrahydroisoquinoline (V), may be isolated, and it is therefore evident that the mechanism of the change at 175° consists in the successive hydrolysis of the two methoxyl groups, followed by hydration of the lactam, forming the corresponding amino-acid (VI), and subsequent decomposition of the latter into carbon dioxide and the amine. The course of the reaction may therefore be represented by the following scheme:

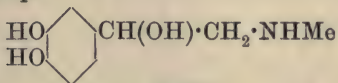


It may be pointed out that the ring fission illustrated above is precisely similar to that occurring in the formation of δ -aminovaleric acid from α -piperidone (Schotten, *Ber.*, 1888, **21**, 2242), whilst the loss of carbon dioxide from the resulting acid is a not uncommon property of hydroxybenzoic acids when under the influence of hydrochloric acid at a high temperature. Proof of the presence of an imino-group in the final product is afforded by the fact that it yields a neutral *triacetyl* derivative,

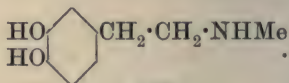


It was found that on increasing the size of the alkyl group on the nitrogen atom, the ring fission and subsequent elimination of carbon dioxide took place with greater difficulty; thus, under the conditions (three hours at 175°) which sufficed to convert 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline almost completely into 3:4-dihydroxyphenylethylmethylamine, the ethyl and propyl homologues were only partly converted into the corresponding 3:4-dihydroxyphenylethylalkylamines, the former giving 30 per cent. and the latter 79 per cent. of the theoretical yield of the corresponding 6:7-dihydroxy-1-keto-2-alkyltetrahydroisoquinoline.

The similarity of structure between the 3:4-dihydroxyphenylethylalkylamines and β -3:4-trihydroxyphenylethylmethylamine (VIII) is obvious; 3:4-dihydroxyphenylethylmethylamine (IX), in fact, differs only from this valuable drug in being devoid of the alcoholic hydroxyl group.



(VIII.)



(IX.)

The physiological action of this compound (and of the others mentioned in this paper) has been examined by Dr. H. H. Dale of the Wellcome Physiological Research Laboratories, to whom the author is indebted for the following report:

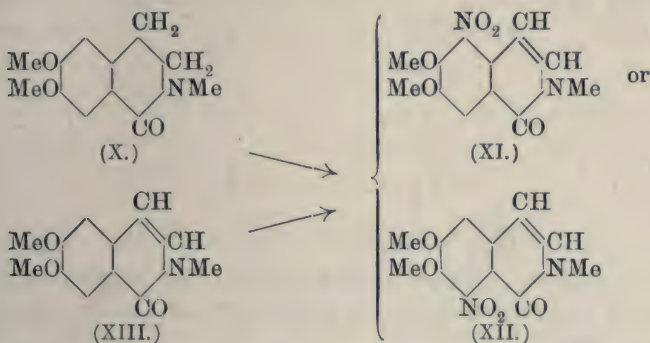
3:4-Dihydroxyphenylethylmethylamine has the characteristic suprarenal action in a high degree, being the nearest in action to the true active principle of any of the large series of related substances which Dr. Dale has now examined; qualitatively there is little difference in the action of the two on organs innervated by sympathetic nerves. The characteristic rise of blood-pressure; acceleration and augmentation of the heart's action; contraction of the pregnant and inhibition of the non-pregnant uterus of the cat; dilatation of the pupil; secretion of saliva—all are produced. A 1 in 1000 solution produced marked and sustained pallor of the conjunctival mucous membrane when instilled into the eye.

Quantitatively, by finding doses which produce rises of blood-

pressure to equal submaximal heights,* Dr. Dale has found that 3:4-dihydroxyphenylethylmethylamine has an activity approximately one-seventh of that of racemic β -3:4-trihydroxyphenylethylmethylamine, or one-tenth of that of the naturally-occurring *lævo*-modification.

The corresponding ethyl- and propyl-amines behave in a similar manner, but to a less extent, the ethylamine having about one-third and the propylamine less than one-twentieth of the activity of the methylamine.†

The valuable properties of 3:4-dihydroxyphenylethylmethylamine suggested the preparation of a trihydroxyphenylethylmethylamine, and it was proposed to prepare such a compound by nitrating 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline, reducing the nitro-compound, substituting a hydroxyl for the amino-group in the usual way, and decomposing the product with hydrochloric acid. This synthesis seemed *a priori* promising, since Freund (*Ber.*, 1887, 20, 2406) has described a nitro-oxyhydrastinine obtained by the action of warm dilute nitric acid on oxyhydrastinine. Unfortunately, the action of this reagent on 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline (X) consisted not only in nitration, but also in simultaneous oxidation, two atoms of hydrogen being removed with the formation of a bright yellow nitro-compound having the formula $C_{12}H_{12}O_5N_2$. This proved to be 5(or 8)-nitro-1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline ‡ (XI or XII), for it was readily obtained by nitrating 6:7-dimethoxy-*N*-methylisoquinolone (XIII) (1-keto-6:7



* The validity and limitations of this method of comparison will be shortly discussed elsewhere in a paper by Barger and Dale.

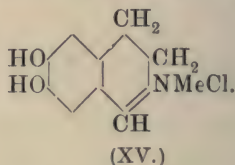
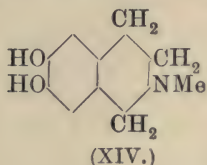
† The parent base, 3:4-dihydroxyphenylethylamine, will shortly be described in a communication to the Society by Barger and Ewins (compare *Trans.*, 1909, 95, footnote to p. 2194).

‡ In view of this result, and since the preparation and properties of this nitro-compound and Freund's "nitro-oxyhydrastinine" are precisely similar, it seems probable that the latter compound is in reality 5(or 8)-nitro-1-keto-6:7-methylenedioxy-2-methyl-1:2-dihydroisoquinoline.

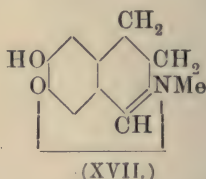
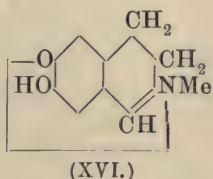
dimethoxy-2-methyl-1:2-dihydroisoquinoline), a compound prepared by Decker and Pschorr (*Ber.*, 1904, **37**, 3401) by the oxidation of *N*-methylisopapaverine.

No further investigation of this compound was made, since 1-keto-2-alkyl-1:2-dihydroisoquinolines do not appear to become converted into phenylethylenealkylamines under the influence of acids at high temperatures; thus, 1-keto-2-methyl-1:2-dihydroisoquinoline can be quantitatively recovered unchanged after heating with hydrochloric acid under pressure for two hours at 170°.

Reference has already been made to the preparation of dihydroxy-bases containing the isoquinoline ring; these are readily obtained in good yield by the action of hydrochloric acid at 175° on the corresponding dimethoxy-compounds; 6:7-dihydroxy-2-methyltetrahydroisoquinoline (XIV) and 6:7-dihydroxy-2-methyl-3:4-dihydroisoquinolinium chloride (XV) have no decided physiological action:

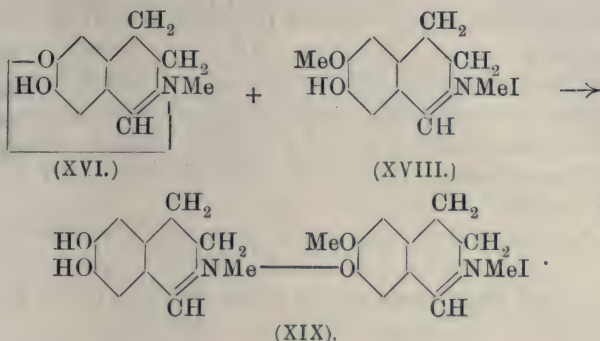


On the addition of sodium carbonate to a solution of the latter compound, the *phenolbetaine* of the corresponding isoquinolinium hydroxide is obtained. This compound has one of the two formulæ (XVI) or (XVII), but no attempt has been made to determine

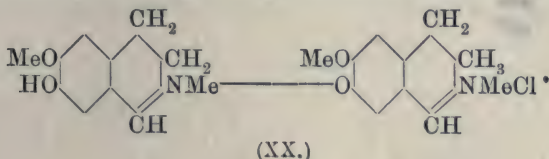


which of the two is correct, although for the purpose of further discussion the former has been arbitrarily adopted throughout this communication.

This base exhibits the characteristic properties of phenolbetaines (compare Decker and Dunant, *Annalen*, 1908, **358**, 296), amongst others that of forming the iodide of the corresponding methoxy-compound, 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3:4-dihydroisoquinolinium iodide (XVIII), when heated with methyl iodide. At the same time, a compound (XIX) of the latter with one molecule of the phenolbetaine is found in accordance with the following scheme:



This compound may be crystallised unchanged, and can be converted into the chloride by means of silver chloride, and crystallised as such without breaking down, but is readily decomposed by hydriodic acid, the compounds from which it was formed being reproduced. Mixed external phenolbetaines of this type do not appear to have been previously observed, but simple external phenolbetaines of the type $\text{HO}\cdot\text{R}\cdot\text{N}^+\text{O}^-\text{R}\cdot\text{N}^+\text{I}^-$ have been obtained by Griess (*Ber.*, 1880, 13, 246) and by Claus and Howitz (*J. pr. Chem.*, 1890, [ii], 42, 222) and their collaborators by the action of ammonia on substituted ammonium iodides of the type $\text{HO}\cdot\text{R}\cdot\text{N}^+\text{I}^-$; a simple external phenolbetaine (XX) of this type can be similarly obtained from 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride (XVIII).



EXPERIMENTAL.

1-Keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline.

By the method of preparation of this compound by simultaneous oxidation and reduction of 4 : 5-dimethoxy-2- β -methylaminoethylbenzaldehyde (*Trans.*, 1909, 95, 1272), only one-half of the original material is transformed into the above substance. It can, however, be prepared in almost theoretical yield from the same material by the method devised by Freund (*Ber.*, 1889, 22, 457) for the conversion of hydrastinine into oxyhydrastinine, namely, by oxidation by permanganate in the presence of alkali.

Two grams of 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride were dissolved in 180 c.c. of water, rendered alkaline by the addition of 20 c.c. of 10 per cent. aqueous sodium hydroxide, and

mixed with a solution of 0.8 gram (a slight excess) of potassium permanganate in 20 c.c. of water. After one hour, the solution was filtered from manganese dioxide, neutralised with dilute sulphuric acid, evaporated to low bulk, and extracted with ether. After evaporation of the solvent, 1.4 grams of pure 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline were obtained, that is, 96 per cent. of the theoretical.

To the description of this compound previously given (*loc. cit.*), the following may be added. It can be distilled under diminished pressure without decomposition, and passes over as a nearly colourless oil, which solidifies on cooling, at $244^{\circ}(\text{corr.})/16$ mm.

It is easily soluble in water, but, on agitating a strong aqueous solution, an unstable *hydrate* separates as a mass of silky needles, which are sparingly soluble in water. When this hydrate is collected and dried for half an hour on porous porcelain, it melts indefinitely at $40\text{--}70^{\circ}$, but on exposure to air for twelve hours becomes anhydrous, has the melting point $126^{\circ}(\text{corr.})$ of the anhydrous base, and is, as before, easily soluble in water.

5-(or 8)-Nitro-1-keto-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline
(XI or XII, p. 267).

Ten grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline were dissolved in a solution of 10 grams of concentrated nitric acid in 30 c.c. of water and heated on the water-bath. The liquor quickly became brown, and then effervesced vigorously with evolution of brown fumes, whilst a quantity of yellow needles continuously separated out. After a few minutes, the liquor was cooled, filtered from the separated crystals, and again heated, this time over a free flame, when a further quantity of crystals were obtained; these operations were again repeated after the addition of another 5 c.c. of concentrated nitric acid, until no further quantity of the crystalline compound could be obtained. The total yield amounted to 6.4 grams.

5 (or 8)-Nitro-6:7-dimethoxy-2-methyl-1:2-dihydroisoquinoline crystallises from glacial acetic acid in fine bright, canary-yellow needles, which begin to soften at about 240° and melt at $244\text{--}245^{\circ}(\text{corr.})$. It is easily soluble in chloroform, fairly easily so in boiling glacial acetic acid or xylene, but almost insoluble in water or the other usual organic solvents:

0.1521 gave 0.3032 CO_2 and 0.0641 H_2O . $\text{C} = 54.4$; $\text{H} = 4.7$.

$\text{C}_{12}\text{H}_{12}\text{O}_5\text{N}_2$ requires $\text{C} = 54.5$; $\text{H} = 4.6$ per cent.

Like Freund's "nitro-oxyhydrastinine" (*loc. cit.*), it is insoluble in dilute acids or weak alkalis, but dissolves in warm aqueous sodium

hydroxide, and is reprecipitated in a gelatinous form on the addition of dilute acids.

The same nitro-compound is readily obtained by warming 1 gram of 1-keto-6 : 7-dimethoxy-2-methyl-1 : 2-dihydroisoquinoline with a mixture of 1 c.c. of concentrated nitric acid and 3 c.c. of water ; the identity of the product of this reaction with that described above follows from the fact that the two products and a mixture of both melt at the same temperature.

7(or 6)-Hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline (IV, p. 265).

Five grams of 1-keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline and 30 c.c. of concentrated hydrochloric acid were heated together under pressure for two hours at 130—135°. The product consisted of a pale brown liquor containing a mass of cream-coloured needles, which formed the hydrochloride of the new base. The solid matter was collected, dissolved in a little hot water, and, after some time, 3.2 grams of the base separated in spear-like crystals, which melted at 200—208°, but contained some quantity of the dihydroxy-base, since they gave a green coloration with aqueous ferric chloride.

After recrystallisation from absolute alcohol, 7(or 6)-hydroxy-1-keto-6(or 7)-methoxy-2-methyltetrahydroisoquinoline forms colourless, glistening, diamond-shaped plates, which soften from 200°, melt at 210° (corr.), and give no coloration with aqueous ferric chloride :

0.1529 gave 0.3562 CO₂ and 0.0864 H₂O. C = 63.5 ; H = 6.3.

0.1555 „ 0.3635 CO₂ „ 0.0880 H₂O. C = 63.8 ; H = 6.3.

C₁₁H₁₃O₃N requires C = 63.8 ; H = 6.3 per cent.

This compound is very sparingly soluble in cold water, sparingly so in hot water or cold alcohol, readily so in hot alcohol, and sparingly or very sparingly so in the other usual organic solvents. It is insoluble in dilute acids, but soluble in aqueous sodium carbonate or ammonia, and dissolves readily in aqueous sodium hydroxide, forming a *sodium* salt which may be obtained as a crystalline mass by evaporating the solution to a very small bulk in a vacuum over sulphuric acid ; this salt is very easily soluble in water or alcohol.

6 : 7-Dihydroxy-1-keto-2-methyltetrahydroisoquinoline (V, p. 265).

Ten grams of 1-keto-6 : 7-dimethoxy-2-methyltetrahydroisoquinoline and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 145—150°. The product consisted of a pale brown liquor containing pale brown needles ; the latter were collected and digested successively with warm water and a little

boiling alcohol. The residue amounted to 3.4 grams of nearly pure dihydroxy-compound, and the alcohol deposited further small quantities of this compound. 6:7-Dihydroxy-1-keto-2-methyltetrahydroisoquinoline crystallises from absolute alcohol in beautiful colourless grains, which show a large number of sharply cut faces. It begins to sinter at about 250°, and melts at 279° (corr.):

0.1504 gave 0.3400 CO₂ and 0.0788 H₂O. C = 61.7; H = 5.9.

0.1555 „ 10.2 c.c. N₂ at 25° and 768 mm. N = 7.4.

C₁₀H₁₁O₃N requires C = 62.1; H = 5.8; N = 7.3 per cent.

This compound is sparingly soluble in boiling water or alcohol, and almost insoluble in these solvents when cold. It is insoluble in dilute acids, but easily soluble in aqueous ammonia, sodium carbonate, or sodium hydroxide, forming yellow solutions which gradually darken on exposure to air. Aqueous suspensions of this substance give, with ferric chloride solution, a faint green coloration, which gradually develops to deep green as the substance dissolves.

3:4-Dihydroxyphenylethylmethylamine (VII, p. 265).

Ten grams of 1-keto-6:7-dimethoxy-2-methyltetrahydroisoquinoline and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 170—175°.* The acid was then removed by distillation under diminished pressure, and the resulting slate-grey crystals of 3:4-dihydroxyphenylethylmethylamine hydrochloride were washed with acetone. The yield amounted to 8.5 grams, that is, 92 per cent. of the theoretical, and the crude product was purified by crystallisation from water containing sulphurous acid.

3:4-Dihydroxyphenylethylmethylamine is liberated in a crystalline form on the addition of ammonia to an aqueous solution of the hydrochloride. It crystallises from absolute alcohol in colourless clusters of transparent spikes, which melt at 188—189° (corr.). It is sparingly soluble in cold water, more easily so in hot water, sparingly so in boiling alcohol, and very sparingly so in cold alcohol and the usual organic solvents:

0.1524 gave 0.3611 CO₂ and 0.1090 H₂O. C = 64.6; H = 8.0.

0.1567 „ 11.0 c.c. N₂ at 17° and 778 mm. N = 8.3.

C₉H₁₃O₂N requires C = 64.6; H = 7.9; N = 8.4 per cent.

Aqueous solutions of the salts of this base give with ferric chloride solution a deep emerald-green coloration, which becomes orange-brown on the addition of aqueous sodium carbonate; such solutions reduce warm aqueous silver nitrate and boiling Fehling's solution; they give no precipitate with aqueous picric acid.

* On opening the tube, a large volume of gases containing a quantity of carbon dioxide escaped.

The *hydrochloride* crystallises from water in long, colourless prisms, which melt at 179—180° (corr.). This salt is anhydrous, and is easily soluble in water or hot alcohol, but somewhat sparingly so in cold alcohol :

0.1505 gave 0.2944 CO₂ and 0.0939 H₂O. C = 53.3 ; H = 7.0.

0.1843 „ 0.1281 AgCl. Cl = 17.2.

C₉H₁₃O₂N.HCl requires C = 53.1 ; H = 6.9 ; Cl = 17.4 per cent.

The *sulphate* crystallises from water in colourless, transparent prisms, which melt to a brown liquid at 289—290° (corr.), after commencing to soften and turn brown several degrees earlier. This salt is anhydrous, and is somewhat sparingly soluble in cold water :

0.1524 gave 0.2779 CO₂ and 0.0905 H₂O. C = 49.7 ; H = 6.6.

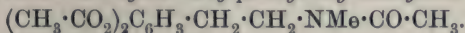
(C₉H₁₃O₂N)₂.H₂SO₄ requires C = 50.0 ; H = 6.5 per cent.

The *oxalate* separates from water in colourless, hexagonal plates, which melt at 194—195° (corr.). This salt is anhydrous, and is sparingly soluble in cold water :

0.1524 gave 0.3168 CO₂ and 0.0938 H₂O. C = 56.7 ; H = 6.9.

(C₉H₁₃O₂N)₂.C₂H₂O₄ requires C = 56.6 ; H = 6.7 per cent.

3 : 4-Diacetoxy-N-acetylphenylethylmethylamine,



Two grams of 3 : 4-dihydroxyphenylethylmethylamine hydrochloride, 5 grams of fused sodium acetate, and 20 c.c. of acetic anhydride were boiled for half an hour under a reflux condenser. The product was stirred into 100 c.c. of water, the resulting clear solution rendered alkaline with sodium carbonate, and extracted with ether. On distilling the ether to low bulk and setting aside, 2.1 grams of the pure compound crystallised out, and a further small quantity was obtained from the mother liquor.

3 : 4-Diacetoxy-N-acetylphenylethylmethylamine crystallises from absolute alcohol in shimmering, hexagonal, monoclinic plates, which soften at 111° and melt at 113—114° (corr.). It is very sparingly soluble in water or dilute acids, but dissolves slowly in dilute aqueous ammonia or sodium hydroxide, giving respectively greenish-yellow and strawberry-red solutions. It is sparingly soluble in cold alcohol or ether :

0.1728 gave 0.3895 CO₂ and 0.1006 H₂O. C = 61.5 ; H = 6.5.

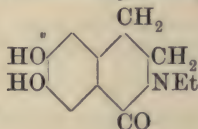
0.1522 „ 6.1 c.c. N₂ at 21° and 775 mm. N = 4.7.

C₁₅H₁₉O₅N requires C = 61.4 ; H = 6.5 ; N = 4.8 per cent.

Action of Hydrochloric Acid at 175° on 1-Keto-6:7-dimethoxy-2-ethyl-tetrahydroisoquinoline.

Four and a-half grams of 1-keto-6:7-dimethoxy-2-ethyltetrahydroisoquinoline and 30 c.c. of concentrated hydrochloric acid were heated together under pressure for three hours at 175°. The resulting clear brown liquor was evaporated to dryness under diminished pressure and dissolved in 15 c.c. of water, when 0·8 gram of 6:7-dihydroxy-1-keto-2-ethyltetrahydroisoquinoline separated in pale brown crystals; after removing these, the process was repeated, when a further quantity of 0·4 gram of the same product was obtained. The mother liquor gave on evaporation 3:4-dihydroxyphenylethylethylamine hydrochloride, of which 1·5 grams were obtained in a pure form by crystallisation from water.

6:7-Dihydroxy-1-keto-2-ethyltetrahydroisoquinoline,

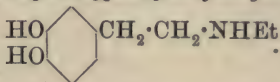


This compound crystallises from absolute alcohol in beautifully crystalline rods, which begin to sinter at about 200°, and melt at 214—215° (corr.). Its chemical properties and solubilities are similar to those of the methyl homologue, with the exception of its solubility in absolute alcohol, which is greater:

0·1524 gave 0·3573 CO₂ and 0·0866 H₂O. C = 63·9; H = 6·4.

C₁₁H₁₃O₃N requires C = 63·8; H = 6·3 per cent.

3:4-Dihydroxyphenylethylethylamine,



The *hydrochloride* crystallises from water in prismatic needles, which melt at 177—178° (corr.). Its chemical properties and solubilities are similar to those of the methyl homologue, except that its aqueous solution does not yield a precipitate of the corresponding base on the addition of ammonia:

0·1519 gave 0·3057 CO₂ and 0·1024 H₂O. C = 55·0; H = 7·6.

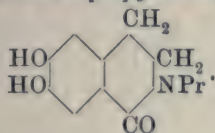
0·1819 „ 0·1239 AgCl. Cl = 16·8.

C₁₀H₁₅O₂N, HCl requires C = 55·1; H = 7·4; Cl = 16·3 per cent.

Action of Hydrochloric Acid at 175° on 1-Keto-6 : 7-dimethoxy-2-propyl-tetrahydroisoquinoline.

Two grams of 1-keto-6 : 7-dimethoxy-2-propyltetrahydroisoquinoline and 15 c.c. of concentrated hydrochloric acid, heated together under pressure for three hours at 175°, and worked up as in the preceding case, gave 1·4 grams of 6 : 7-dihydroxy-1-keto-2-propyltetrahydroisoquinoline and 0·4 gram of 3 : 4-dihydroxyphenylethylpropylamine hydrochloride.

6 : 7-Dihydroxy-1-keto-2-propyltetrahydroisoquinoline,

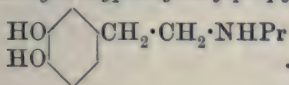


This compound separates from absolute alcohol in oblong, rectangular plates, which melt at 184—185° (corr.). Its chemical properties and solubilities are similar to those of the ethyl homologue :

0·1548 gave 0·3677 CO₂ and 0·0959 H₂O. C = 64·8 ; H = 6·9.

C₁₂H₁₅O₃N requires C = 65·1 ; H = 6·9 per cent.

3 : 4-Dihydroxyphenylethylpropylamine,



The *hydrochloride* crystallises from water in clusters of transparent, irregular prisms, which melt at 184—185° (corr.). Its chemical properties and solubilities are similar to those of the ethyl homologue :

0·1540 gave 0·3200 CO₂ and 0·1091 H₂O. C = 56·7 ; H = 7·9.

C₁₁H₁₇O₂N, HCl requires C = 57·0 ; H = 7·9 per cent.

6 : 7-Dihydroxy-2-methyltetrahydroisoquinoline (XIV, p. 268).

Eight and a-half grams of 6 : 7-dimethoxy-2-methyltetrahydroisoquinoline hydrochloride (containing 3 molecules of water of crystallisation) and 30 c.c. of concentrated hydrochloric acid were heated in a sealed tube for five hours at 170°. On cooling, 4·7 grams of 6 : 7-dihydroxy-2-methyltetrahydroisoquinoline hydrochloride separated in grey needles, that is, 76 per cent. of the theoretical.

6 : 7-Dihydroxy-2-methyltetrahydroisoquinoline separates on the addition of sodium carbonate to an aqueous solution of the hydrochloride. It crystallises from water in nearly colourless (pale buff)

needles, which melt at 221—222° (corr.), and contain one molecule of water of crystallisation. It is very sparingly soluble in water and the usual organic solvents.

Aqueous solutions of its salts give with ferric chloride a deep green coloration, which becomes mauve on the addition of sodium carbonate. They reduce hot silver nitrate and also boiling Fehling's solution :

0.1833 * lost 0.0172 at 100°. $\text{H}_2\text{O} = 9.4$.

0.1500 † gave 0.3693 CO_2 and 0.0987 H_2O . $\text{C} = 67.1$; $\text{H} = 7.4$.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 9.1$ per cent.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 67.0$; $\text{H} = 7.3$ per cent.

The *hydrochloride* crystallises from water in colourless needles, which are anhydrous and melt at 277° (corr.). It is fairly easily soluble in water, but sparingly so in alcohol :

0.1522 gave 0.3093 CO_2 and 0.0937 H_2O . $\text{C} = 55.4$; $\text{H} = 6.9$.

0.1721 „ 0.1144 AgCl . $\text{Cl} = 16.4$.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}, \text{HCl}$ requires $\text{C} = 55.7$; $\text{H} = 6.6$; $\text{Cl} = 16.4$ per cent.

The *picrate* crystallises from alcohol in transparent, yellow, monoclinic (hexagonal) plates, which melt at 191—192° (corr.).

Phenolbetaine of 6 : 7-Dihydroxy-2-methyl-3 : 4-dihydroisoquinolinium Hydroxide (XVI or XVII, p. 268).

Ten grams of 6 : 7-dimethoxy-2-methyl-3 : 4-dihydroisoquinolinium chloride and 60 c.c. of concentrated hydrochloric acid were heated together under pressure for four hours at 170°. The product was evaporated to dryness under diminished pressure, and the crystalline residue well washed with acetone. 6.5 Grams of nearly pure anhydrous 6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinolinium chloride were obtained, the yield thus amounting to 93 per cent. of the theoretical.

The *phenolbetaine* of 6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinolinium hydroxide separates in long, deep yellow needles containing one and a-quarter molecular proportions of water of crystallisation on the addition of the calculated quantity of aqueous sodium hydroxide, or an excess of sodium carbonate to a strong solution of its chloride :

0.1816 * lost 0.0201 at 100°. $\text{H}_2\text{O} = 11.1$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}, 1\frac{1}{4}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.3$ per cent.

After recrystallisation from moist alcohol it forms deep yellow, monoclinic plates, which melt to a reddish-black liquid, decompose at 222° (corr.), and contain 1 molecule of water of crystallisation :

0.1543 * gave 0.2667 CO_2 and 0.0746 H_2O . $\text{C} = 61.5$; $\text{H} = 7.0$.

* Air-dried.

† Dried at 100°.

0.1380 * gave 0.3096 CO_2 and 0.0839 H_2O . $\text{C} = 61.2$; $\text{H} = 6.8$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}, \text{H}_2\text{O}$ requires $\text{C} = 61.5$; $\text{H} = 6.8$ per cent.

0.1388 † gave 0.3448 CO_2 and 0.0795 H_2O . $\text{C} = 67.7$; $\text{H} = 6.4$.

$\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{C} = 67.8$; $\text{H} = 6.3$ per cent.

The phenolbetaine crystallises from absolute alcohol in anhydrous, yellowish-brown, serrated spikes, which have the same melting point as the hydrated base, is moderately easily soluble in cold water, not more so in aqueous sodium carbonate or ammonia, but readily in dilute acids or aqueous sodium hydroxide. It is rather sparingly soluble in cold alcohol or chloroform, and very sparingly so in the other usual organic solvents. Aqueous solutions of its salts give with aqueous ferric chloride a deep green coloration, and on the subsequent addition of sodium carbonate yield a pale reddish-brown suspension, the supernatant liquor appearing a dull yellow after the settlement of the ferric hydroxide. Aqueous solutions of the salts of this base reduce hot silver nitrate, but do not reduce Fehling's solution even on boiling.

The *chloride* crystallises from moist acetone in primrose needles, which contain one and a-half molecular proportions of water of crystallisation. After drying at 100° , this salt melts and decomposes at 276° (corr.). It is easily soluble in water, but sparingly so in alcohol:

0.4060, air-dried salt, lost 0.0437 at 100° . $\text{H}_2\text{O} = 10.8$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 11.2$ per cent.

0.1468 † gave 0.3019 CO_2 and 0.0743 H_2O . $\text{C} = 56.1$; $\text{H} = 5.7$.

0.1593 † „ 0.1081 AgCl . $\text{Cl} = 16.8$.

$\text{C}_{10}\text{H}_{12}\text{O}_2\text{NCl}$ requires $\text{C} = 56.2$; $\text{H} = 5.7$; $\text{Cl} = 16.6$ per cent.

The *picrate* crystallises from alcohol in yellow, transparent, irregular plates, which melt and decompose at 236° (corr.).

The *sodium* salt separates in clusters of beautiful crimson needles on the addition of alcohol to a solution of the phenolbetaine in the calculated quantity of 2*N*-aqueous sodium hydroxide. It is easily soluble in water or alcohol. This salt contains 6 molecules of water of crystallisation, of which five are lost after prolonged heating at 120° :

0.2530 * gave 0.0562 Na_2SO_4 . $\text{Na} = 7.2$.

0.2541 * lost 0.0763 at 120° . $\text{H}_2\text{O} = 30.0$.

$\text{C}_{10}\text{H}_{10}\text{O}_2\text{NNa}, 6\text{H}_2\text{O}$ requires $\text{Na} = 7.5$; loss of $5\text{H}_2\text{O} = 29.3$ per cent.

Action of Methyl Iodide on the Phenolbetaine of 6 : 7-Dihydroxy-2-methyl-3 : 4-dihydroisoquinolinium Hydroxide.

Eight grams of the phenolbetaine, which had been dried for some time at 100° , were heated together with 16 grams of methyl iodide for

* Air-dried.

† Dried at 100° .

three hours at 100°. The crystalline product obtained was separated by fractional crystallisation from absolute alcohol into:

(1) 7.2 grams of 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium iodide, melting at 213° (corr.).

(2) 2.0 grams of 6(or 7)-methoxy-7(or 6)-[6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinoliniumoxy]-2-methyl-3 : 4-dihydroisoquinolinium iodide, melting at 181—182° (corr.), and

(3) a small quantity of a brown, gummy residue.

In a second experiment, in which the phenolbetaine was not previously dried at 100°, a larger proportion of the latter compound was obtained, 11 grams of hydrated phenolbetaine and 25 grams of methyl iodide yielding 4.4 grams of the first-mentioned iodide and 5.1 grams of the latter, besides an oily residue which was neglected.

7(or 6)-Hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium Salts (XVIII, p. 269).

The *iodide* crystallises from alcohol in fine long, golden needles, which melt and decompose at 218° (corr.). It is anhydrous, and is sparingly soluble in water or alcohol :

0.1536 gave 0.2336 CO₂ and 0.0611 H₂O. C = 41.5 ; H = 4.5.

0.1876 „ 0.1370 AgI. I = 39.5.

0.3046 „ by Zeisel's method 0.2098 AgI. OMe = 9.1.

C₁₁H₁₄O₂NI requires C = 41.4 ; H = 4.4 ; I = 39.8 ; OMe = 9.7 per cent.

The *chloride* was obtained from the iodide by double decomposition with silver chloride. It crystallises from aqueous acetone in yellow needles, which contain one molecule of water of crystallisation, and effervesce at 155° (corr.), after sintering from about 140°; after drying at 100°, it decomposes at 198° (corr.). It is easily soluble in water or hot alcohol, and its aqueous solution gives no coloration with ferric chloride solution :

0.2011 * lost 0.0146 at 100°. H₂O = 7.3.

C₁₁H₁₄O₂NCl.H₂O requires H₂O = 7.3 per cent.

0.1400 † gave 0.2970 CO₂ and 0.0815 H₂O. C = 57.9 ; H = 6.5.

0.1818 † „ 0.1134 AgCl. Cl = 15.4

C₁₁H₁₄O₂NCl requires C = 58.0 ; H = 6.2 ; Cl = 15.6 per cent.

On dissolving this salt in warm concentrated aqueous ammonia, a deep red solution is obtained, which deposits, on cooling, orange crystals of the chloride of the external phenolbetaine, namely, 6(or 7)-methoxy-7(or 6)-[7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinoliniumoxy]-2-methyl-3 : 4-dihydroisoquinolinium chloride (XX, p. 269).

After recrystallisation from absolute alcohol, this salt forms bright

* Air-dried.

† Dried at 100°.

orange prisms, which contain $3\frac{1}{2}\text{H}_2\text{O}$ and melt and decompose at 135° (corr.). It is easily soluble in water, but sparingly so in cold absolute alcohol; it contains chlorine. On heating this salt at 100° , it first becomes crimson, and then melts to a deep red gum which retains about 1 per cent. of water of crystallisation:

0.1413 * gave 0.2831 CO_2 and 0.0933 H_2O . $\text{C} = 54.6$; $\text{H} = 7.3$.

0.1193 * lost 0.0146 at 100° . $\text{H}_2\text{O} = 12.2$.

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}_2\text{Cl} \cdot 3\frac{1}{2}\text{H}_2\text{O}$ requires $\text{C} = 54.8$; $\text{H} = 7.1$; $\text{H}_2\text{O} = 13.1$ per cent.

0.1047 † gave 0.2397 CO_2 and 0.0624 H_2O . $\text{C} = 62.4$; $\text{H} = 6.6$.

$\text{C}_{22}\text{H}_{27}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{C} = 63.1$; $\text{H} = 6.5$ per cent.

6(or 7)-Methoxy-7(or 6)-[6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinoliniumoxy]-2-methyl-3 : 4-dihydroisoquinolinium Salts (XIX, p. 269).

The *iodide* crystallises from absolute alcohol in hard, orange grains, which melt and decompose at 181 — 182° (corr.). It is anhydrous and easily soluble in water, but sparingly so in cold alcohol. Its aqueous solution gives a deep green coloration with ferric chloride solution:

0.1524 gave 0.2826 CO_2 and 0.0713 H_2O . $\text{C} = 50.6$; $\text{H} = 5.2$.

0.1867 „ 0.0896 AgI . $\text{I} = 25.9$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{I}$ requires $\text{C} = 50.8$; $\text{H} = 5.1$; $\text{I} = 25.6$ per cent.

On adding a molecular proportion of hydriodic acid to the deep orange aqueous solution of 2 grams of this salt, a pale yellow solution was obtained. On evaporating this to low bulk and adding absolute alcohol, 0.9 gram of 7(or 6)-hydroxy-6(or 7)-methoxy-2-methyl-3 : 4-dihydroisoquinolinium iodide separated; after recrystallisation, this melted at 218° (corr.), both alone and when mixed with the pure salt, and gave no coloration with aqueous ferric chloride. On then adding ammonia to the mother liquor, a small quantity of the phenolbetaine of 6 : 7-dihydroxy-2-methyl-3 : 4-dihydroisoquinolinium hydroxide separated; after recrystallisation from alcohol, this compound melted at 222° (corr.), and its melting point suffered no depression when the compound was mixed with the pure phenolbetaine.

The *chloride* was prepared from the iodide by double decomposition with silver chloride. It crystallises from absolute alcohol in deep yellow, glistening prisms, which melt at 186 — 187° (corr.), and contain one molecule of water of crystallisation:

0.3360 * lost 0.0169 at 100° . $\text{H}_2\text{O} = 5.0$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{Cl} \cdot \text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 4.3$ per cent.

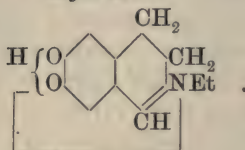
0.1416 † gave 0.3251 CO_2 and 0.0810 H_2O . $\text{C} = 62.6$; $\text{H} = 6.4$.

$\text{C}_{21}\text{H}_{25}\text{O}_4\text{N}_2\text{Cl}$ requires $\text{C} = 62.3$; $\text{H} = 6.2$ per cent.

* Air-dried.

† Dried at 100° .

Phenolbetaine of 6 : 7-dihydroxy-2-ethyl-3 : 4-dihydroisoquinolinium Hydroxide,



The preparation and properties of this compound and its salts are similar to those of the corresponding methyl-homologue.

The *phenolbetaine of 6 : 7-dihydroxy-2-ethyl-3 : 4-dihydroisoquinolinium hydroxide* crystallises from absolute alcohol in deep yellow rods, which melt and decompose at 235° (corr.). It is anhydrous :

0.1442 gave 0.3661 CO₂ and 0.0919 H₂O. C = 69.2 ; H = 7.1.

C₁₁H₁₃O₂N requires C = 69.1 ; H = 6.9 per cent.

The *chloride* crystallises from water in fine yellow needles, which melt at 104° (corr), and contain 2 molecules of water of crystallisation. After drying at 100°, this salt melts and decomposes at 201—202° (corr.) :

0.2170 * lost 0.0300 at 100°. H₂O = 13.8.

C₁₁H₁₄O₂NCl.2H₂O requires H₂O = 13.7 per cent.

0.1517 † gave 0.3221 CO₂ and 0.0845 H₂O. C = 58.0 ; H = 6.2.

0.1475 † „ 0.0943 AgCl. Cl = 15.8.

C₁₁H₁₄O₂NCl requires C = 58.0 ; H = 6.2 ; Cl = 15.6 per cent.

The *picrate* crystallises from alcohol in clusters of golden, spear-like needles, which melt and decompose at 191° (corr.).

THE WELLCOME CHEMICAL WORKS
DARTFORD, KENT.

XXIX.—The Absorption Spectra of Naphthalene and of Tetramethylnaphthalene.

BY ANNIE HOMER and JOHN EDWARD PURVIS.

IN a paper on the absorption spectra of the hydrocarbons isolated from the products of the action of aluminium chloride on naphthalene (Homer and Purvis, Trans., 1908, 93, 1319), we described the absorption spectrum of a substance having the empirical formula C₁₄H₁₆. From chemical considerations it had been suggested that

* Air-dried.

† Dried at 100°.

this hydrocarbon was an alkyl, probably a tetramethyl, derivative of naphthalene, and it was thought that a comparison of the absorption spectrum of this hydrocarbon with that of naphthalene would furnish additional evidence as to its constitution.

Hartley, in his earlier work (Trans., 1881, 29, 153), showed that the absorption spectrum of naphthalene was characterised by four bands in the ultraviolet region of the spectrum. In a later paper, Hartley (Trans., 1885, 47, 685) showed that there were four bands, the positions of which differed from those of the earlier observations. The method employed by Hartley differed from that used by us, and described in the previous paper (*loc. cit.*). For purposes of comparison it was necessary for us to study the absorption spectrum of naphthalene under the same experimental conditions as those employed in the study of the hydrocarbons under investigation. Our results showed that for $N/1000$ -solutions in alcohol, the absorption curve for naphthalene, as observed by Hartley in his first paper, showed four characteristic bands. The mean oscillation frequencies of these bands did not coincide with those given by Hartley, but we did not comment on the discrepancies at the time of our previous work. The curve for $N/1000$ -solutions of the hydrocarbon $C_{14}H_{16}$ also showed four bands, similar in character to the naphthalene bands, although less persistent and further shifted towards the red end of the spectrum (Fig. 1).

The mean oscillation frequencies of the bands were :

For naphthalene, Hartley, first paper	3508	3690	3840	3921
" " second paper ...	3211	3273	3369	3849
" Homer and Purvis (not previously published)..	3500	3620	3765	3900
For $C_{14}H_{16}$, Homer and Purvis	3434	3562	3680	3776

From these results we concluded that the substance $C_{14}H_{16}$ was probably tetramethylnaphthalene, as had been previously suggested (Homer, Trans., 1907, 91, 1103).

Since the publication of these results, Baly and Tuck (Trans., 1908, 93, 1902), in their work on the absorption spectra of aromatic hydrocarbons, have shown that for naphthalene there are three characteristic bands having mean oscillation frequencies : $1/\lambda = 3125$, $1/\lambda = 3220$, and $1/\lambda = 3700$. The bands $1/\lambda = 3125$ and $1/\lambda = 3220$ only appear in strong solutions or in proportionately greater thicknesses of dilute solutions. The band $1/\lambda = 3700$ is a broad band, and corresponds with the four bands observed by Hartley in his first paper (Trans., 1881, 39, 153) and also by us.

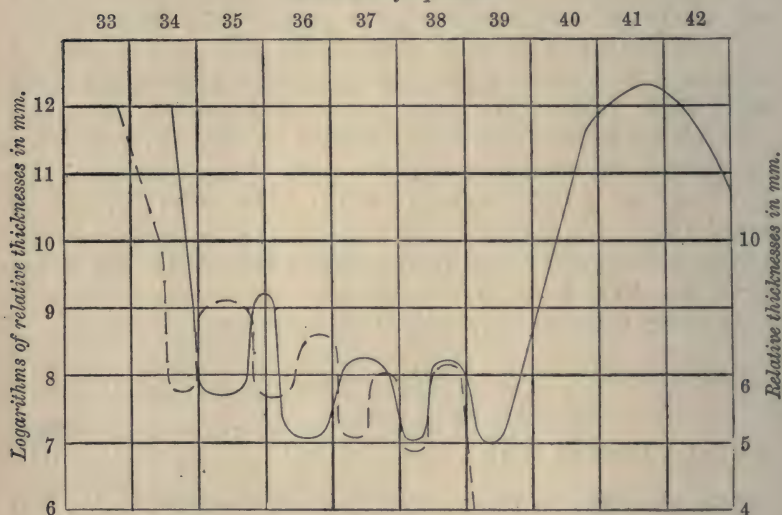
After reading Baly and Tuck's paper, it seemed necessary for us to re-examine the absorption spectrum of the hydrocarbon $C_{14}H_{16}$. For if, as we had previously surmised, the hydrocarbon $C_{14}H_{16}$ is a tetra-

methyl derivative of naphthalene, there should be indications of bands corresponding with the naphthalene bands, $1/\lambda$ 3125 and $1/\lambda$ 3220, observed by Baly and Tuck. The absence of such bands would, according to these observers, point to a difference between the constitution of naphthalene and of the hydrocarbon $C_{14}H_{16}$.

At the time of our previous experiments we had only sufficient of the hydrocarbon with which to make a $N/1000$ -solution. This strength was compared with a similar $N/1000$ -solution of naphthalene. These solutions gave the four bands already described, and corresponding with the broad band, $1/\lambda$ 3700, of Baly and Tuck. Since then the

FIG. 1.

Oscillation frequencies.

Full curve : $N/1000$ -solution of naphthalene in alcohol.Dash ,, : $N/1000$ -solution of $C_{14}H_{16}$ in alcohol.

hydrocarbon has been made in larger quantity, and we have been able to compare its $N/10$ -solution with a similar solution of naphthalene. The results have been plotted in the accompanying curves (Fig. 2).

It will be seen from a glance at the curves, that for $N/10$ -solution of naphthalene there are two bands similar to those obtained by Baly and Tuck. The curve for the hydrocarbon $C_{14}H_{16}$ also shows two similar bands, less persistent and further shifted towards the red end of the spectrum than the naphthalene bands.

The mean oscillation frequencies of the bands are :

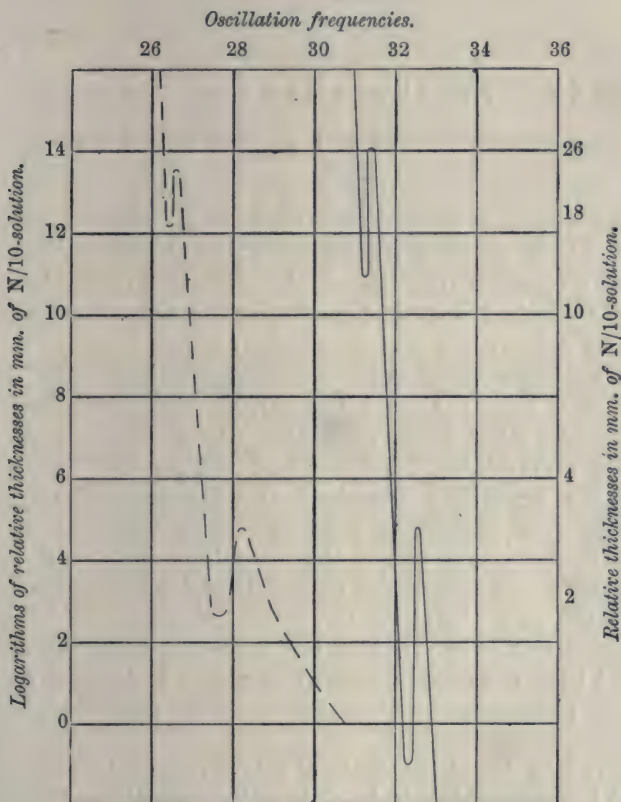
Naphthalene, Baly and Tuck	3125	3220
,, $N/10$ -solution, Homer and Purvis ...	3122	3225
$C_{14}H_{16}$, $N/10$ -solution, ,, ,, ,, ...	2638	2770

The results of our investigation may be summarised as follows :

I. The absorption curves for both $N/1000$ - and $N/10$ -solutions of the hydrocarbon $C_{14}H_{16}$ are similar to the curves for naphthalene. These results are in accordance with our previous suggestion that the substance is a tetramethyl derivative of naphthalene.

II. Our experiments confirm the observation of Baly and Tuck

FIG. 2.



Full curve : $N/10$ -solution of naphthalene in alcohol.
 Dash „ : $N/10$ -solution of $C_{14}H_{16}$ in alcohol.

with regard to the presence of bands corresponding with $1/\lambda$ 3125 and $1/\lambda$ 3220 in naphthalene and its derivative.

III. Hartley in his first paper represented the naphthalene curve for dilute solutions as being characterised by the presence of four narrow bands. Baly and Tuck from their results consider that there is only one broad band, $1/\lambda$ 3700, which corresponds with Hartley's

four bands. The curves obtained by us for $N/1000$ -solutions of naphthalene, and of its derivative, $C_{14}H_{16}$, shows four narrow bands. These observations support Hartley's first interpretation of the absorption curve of naphthalene.

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XXX.—*The Alkaloids of Ergot. Part II.*

By GEORGE BARGER and ARTHUR JAMES EWINS.

IN a previous communication on this subject (Trans., 1907, **91**, 337), one of us, in conjunction with F. H. Carr, described the new amorphous alkaloid ergotoxine, $C_{35}H_{41}O_6N_5$, and assigned to Tanret's crystalline ergotinine the formula $C_{35}H_{39}O_5N_5$. The crystalline alkaloid was thus proved to be the anhydride of the amorphous one, as was first surmised by Kraft.*

The transformation of ergotoxine into ergotinine takes place by boiling with methyl alcohol (Kraft), or with acetic anhydride. When, on the other hand, ergotinine was warmed on the water-bath with very dilute phosphoric acid, Barger and Carr obtained from it the crystalline phosphate of an amorphous base, which closely resembled ergotoxine phosphate in physiological action and had the same melting point; the crystalline form was, however, entirely different. Ergotoxine phosphate crystallises in thin needles (Fig. 2), the new phosphate formed rhomb-shaped, triangular, or hexagonal plates (Fig. 1), and the difference persisted after the bases had been liberated, dissolved in ether, and again converted into their phosphates by precipitation with alcoholic phosphoric acid.

We have now found the cause of this difference between the two salts. When ergotinine is heated with a solution of phosphoric acid in ethyl alcohol, there is formed, not ergotoxine phosphate, but the phosphate of ergotoxine ethyl ester, and it is the latter salt which crystallises in plates. The hydrochlorides of the two bases are also quite different (Figs. 3 and 4). That the new base

* The identity of Kraft's hydroergotinine (*Arch. Pharm.*, 1906, **244**, 336) with ergotoxine was recently doubted by Vahlen (*Arch. exp. Path. Pharm.*, 1908, **60**, 42) on physiological grounds, but an analysis of hydroergotinine sulphate by Kraft (*Arch. Pharm.*, 1907, **245**, 644) and a comparative physiological examination by Dale (*Arch. exp. Path. Pharm.*, 1909, **61**, 113) leave no doubt that hydroergotinine and ergotoxine are synonymous terms.

is an ethyl ester was shown by analysis, and especially by a determination of the ethoxy-group by Zeisel's method.

It thus follows that ergotoxine contains a carboxyl group, and that ergotinine is its lactone (or lactam). In accordance with this view, ergotoxine is soluble in sodium hydroxide, but ergotinine is not, nor is the ester-base above referred to. Esterification probably takes place to some extent when ergotoxine is boiled with alcohol (in the absence of phosphoric acid). We have noticed repeatedly in converting ergotoxine into ergotinine by boiling with methyl alcohol (Kraft's method) that the yield is far from quantitative; some of the ergotoxine is probably converted by this process into the very soluble ethyl ester, instead of the crystalline anhydride. It is, moreover, quite likely that ergotinine itself when boiled with alcohol forms ergotoxine ester to some extent; this behaviour would explain the loss of ergotoxine on recrystallisation which we ourselves and others (Tanret, Meulenhoff) have noticed. The fall in optical rotation shown by alcoholic ergotinine solutions, especially on boiling, is also probably due to the formation of an ergotoxine ester.

Besides proving the presence of a carboxyl group in ergotoxine, we have been able to establish the presence of a somewhat larger and more characteristic fragment of the complicated molecule of the ergot alkaloids. On destructive distillation, both ergotoxine and ergotinine yield a small quantity of a crystalline substance, and this we have been able to identify as *isobutyrylformamide*, $\text{CHMe}_2 \cdot \text{CO} \cdot \text{CO} \cdot \text{NH}_2$. The yield of this substance is only 5 per cent. of the (very costly) alkaloid employed; as we had only a few decigrams of the substance at our disposal, its identification was somewhat troublesome, but was finally rendered certain by direct comparison with a specimen of *isobutyrylformamide* synthesised for the purpose.

A ketonic amide of this type does not appear to have been previously obtained from a natural substance, and we are unable to suggest the mechanism of its formation from the ergot alkaloids. We do not think, however, that either of the oxygen atoms of the amide belongs to the carboxyl group which we have shown to be present in ergotoxine. If this be admitted, we have accounted for four out of the six oxygen atoms of that alkaloid (or three out of the five present in ergotinine). The two remaining oxygen atoms are not present as phenolic hydroxy- or methoxy-groups, because ergotinine is insoluble in sodium hydroxide, and when examined by Zeisel's method yields a negative result. One of the nitrogen atoms probably has a methyl group attached to it, because some-

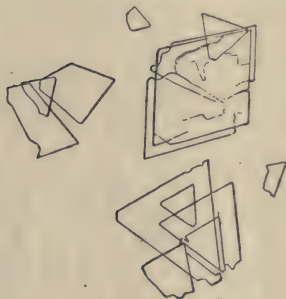
thing like one equivalent of methyl iodide is set free when ergotinine is examined by Herzig and Meyer's method. At least one of the five nitrogen atoms is tertiary, for a methiodide is slowly formed. It is remarkable that, in spite of having five nitrogen atoms, the ergot alkaloids are only very feeble mono-acid bases.

EXPERIMENTAL.

Phosphate of Ergotoxine Ethyl Ester, $C_{34}H_{40}O_4N_5 \cdot CO_2 \cdot C_2H_5, H_3PO_4$.

One gram of crystalline ergotinine was suspended in 10 c.c. of absolute ethyl alcohol; and 1.1 equivalent of phosphoric acid dissolved in 5 c.c. of alcohol was added. On warming on the water-bath for fifteen to thirty minutes, the ergotinine gradually dissolved; on cooling, an amorphous solid separated, which was collected and crystallised from 90—95 per cent. ethyl alcohol. In this way about 0.3 gram of a grey product was obtained, which

FIG. 1.



Phosphate of ergotoxine ethyl ester.
× 65 diameters.

FIG. 2.



Ergotoxine phosphate.
× 65 diameters.

on recrystallisation from 12 c.c. of 95 per cent. alcohol separated in almost white leaflets (Fig. 2), melting at $187-188^\circ$ (bath previously heated to 180°). For the sake of comparison the crystalline form of ergotoxine phosphate is shown in Fig. 2. These and the other figures were drawn from micro-photographs:

0.1353 gave 0.2922 CO_2 and 0.0812 H_2O . $C = 58.9$; $H = 6.4$.

$C_{37}H_{45}O_6N_5, H_3PO_4$ requires $C = 58.9$; $H = 6.4$ per cent.

$C_{35}H_{41}O_6N_5, H_3PO_4$ „ $C = 57.9$; $H = 6.1$ „

As the phosphate of an ethyl ester of ergotoxine contains only 1 per cent. more carbon than that of the corresponding ergotoxine salt, a direct determination of the ethoxy-group was made by Zeisel's method:

0.3503 gave 0.1064 AgI. $\text{OEt} = 5.82$.

$\text{C}_{34}\text{H}_{40}\text{O}_4\text{N}_5 \cdot \text{CO}_2\text{Et}, \text{H}_3\text{PO}_4$ requires $\text{OEt} = 5.97$ per cent.

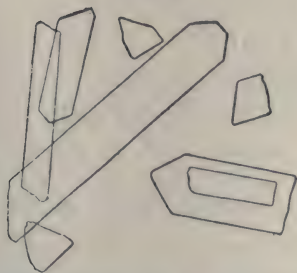
The rotation of this salt was also determined in 75 per cent. alcohol. $l = 1$ dcm.; $c = 2.03$; $\alpha_D + 1.58^\circ$; $[\alpha]_D + 77.8^\circ$. From the phosphate obtained in the manner described, the base was set free by sodium carbonate, dissolved in ether, and dried with sodium sulphate. From the ethereal solution of the base obtained in this way, the hydrochloride and the oxalate were precipitated by adding alcoholic hydrochloric acid and ethereal oxalic acid solutions respectively.

Hydrochloride of Ergotoxine Ethyl Ester, $\text{C}_{37}\text{H}_{45}\text{O}_6\text{N}_5 \cdot \text{HCl}$.

The precipitated salt crystallised from 90 per cent. alcohol in large plates (Fig. 3), which melted at $206\text{--}207^\circ$ (bath previously heated to 190°). For the sake of comparison, crystals of ergotoxine hydrochloride (m. p. 205°) are shown in Fig. 4.*

The difference in crystalline form existing between salts of ergotoxine and the corresponding salts of the ethyl ester is also clearly shown in the case of the oxalates formed by adding an

FIG. 3.



Hydrochloride of ergotoxine ethyl ester.
× 65 diameters.

FIG. 4.



Ergotoxine hydrochloride.
× 65 diameters.

ethereal solution of oxalic acid to the bases dissolved in ether. Both salts melt at $179\text{--}180^\circ$, but whereas the ergotoxine oxalate forms elongated, rectangular prisms, the salt of the ester crystallises in hexagonal leaflets.

By warming ergotinine with a solution of phosphoric acid in methyl alcohol, crystalline salts of ergotoxine methyl ester are readily obtainable. As in the case of the ethyl ester, this base is

* In the previous paper (Trans., 1907, **81**, 350) it was stated that ergotoxine hydrochloride forms "diamond-shaped plates and very thin and very long, square-ended needles." The plates, however, were an admixture of the hydrochloride of ergotoxine ethyl ester.

amorphous, thus resembling ergotoxine; the ester bases differ, however, from ergotoxine in being insoluble in dilute sodium hydroxide.

Salts of Ergotoxine.

In addition to the phosphate, the hydrochloride, and the two oxalates of ergotoxine, which were described in the earlier paper, several other salts have been obtained crystalline. They were prepared in each case by adding a dilute ethereal or alcoholic solution of the acid to a solution of ergotoxine in ether, until no further precipitate was formed. The precipitated salt was dried in a vacuum, and crystallised from warm 90 to 95 per cent. alcohol. Not infrequently the salt separates as a jelly on cooling; in such cases it is best to dilute the solution, so that nothing separates on cooling, and then to add a few drops of dry ether at intervals.

Ergotoxine picrate forms pale yellow, acicular prisms, melting at 214—215° (bath first heated to 210°):

0.1536 gave 17.2 c.c. N_2 (moist) at 10.5° and 757 mm. $N=13.2$.

$C_{35}H_{41}O_6N_5, C_6H_3O_7N_3$ requires $N=13.1$ per cent.

Ergotoxine hydrobromide, acicular prisms, melting at 208°:

0.1042 gave 0.0260 AgBr. $Br=10.6$.

$C_{35}H_{41}O_6N_5, HBr$ requires $Br=11.3$ per cent.

Ergotoxine sulphate, prisms, melting at 197°:

0.1192 gave 0.0358 $BaSO_4$. $H_2SO_4=12.6$.

$C_{35}H_{41}O_6N_5, H_2SO_4$ requires $H_2SO_4=13.5$ per cent.

This appears to be a somewhat impure acid sulphate; that prepared by Kraft was the normal one.

Ergotoxine nitrate forms short, broad prisms, melting at 193—194°.

Action of Methyl Iodide on Ergotinine, Ergotoxine, and Ergotoxine Esters.

Ergotinine and allied bases appear to have one tertiary nitrogen atom. Ergotinine dissolves readily in methyl iodide, but when the solution is left at the laboratory temperature for some days, it is gradually transformed into a white jelly, readily soluble in alcohol; this jelly doubtless represents the methiodide. Ergotoxine and its esters behave in a similar way, except that the reaction is more rapid. In no case, however, could a crystalline product be isolated. We give as an example the analysis of the precipitate formed in a solution of ergotoxine methyl ester in methyl iodide; the substance, presumably the methiodide, was washed with dry ether and dried at 100°:

0.1300 gave 0.0365 AgI. $I=15.2$.

$C_{36}H_{42}O_6N_5, CH_3I$ requires $I=16.2$ per cent.

Action of Absolute Alcohol on Ergotinine.

A solution of 0.24 gram of crystalline ergotinine in 100 c.c. of absolute ethyl alcohol was divided into two portions. A 2.2-dcm. polarimeter tube was filled with one portion of the solution, and kept in the dark at the laboratory temperature for some months. During this time the rotation gradually decreased, as shown by the following table:

	α_D .	l .	$[\alpha]_D$.
June 11th	+1.76°	2.2 dcm.	+333°
June 12th	+1.71	2.2 „	+324
June 14th	+1.66	2.2 „	+314
June 17th	+1.61	2.2 „	+305
June 28th	+1.61	2.2 „	+305
July 19th	+1.52	2.2 „	+290
Sept. 13th	+0.62	1 „	+258

The other portion was heated under a reflux condenser on the water-bath; here the change was more rapid:

Time in hours.	α_D .	l .	$[\alpha]_D$.
0	+1.76°	2.2 dcm.	+333°
1	+1.59	2 „	+331
4	+1.41	2 „	+294
8½	+0.67	2 „	+275
15½	+0.61	1 „	+254
23	+0.59	1 „	+246
30	+0.48	1 „	+200
37	+0.37	1 „	+154

In boiling alcoholic solution the change is even more rapid. A saturated solution prepared by shaking at 10° gave:

$l=2.2$ dcm.; $c=0.2566$; $\alpha_D+1.91^\circ$; $[\alpha]_D+338^\circ$.

After boiling for five minutes, $[\alpha]_D$ fell to 327°, after one hour to 300°, after three hours to 242°.

Crystals of ergotinine, obtained by rapidly cooling a boiling alcoholic solution, are shown below:

FIG. 5.



Ergotinine. $\times 65$ diameters.

Isolation of isoButyrylformamide on Destructive Distillation of the Ergot Alkaloids.

The formation of a crystalline sublimate can be observed by carefully heating a few milligrams of ergotinine or ergotoxine in a small tube. The alkaloids melt and decompose, and a minute quantity of a colourless liquid appears in the cold part of the tube; this soon crystallises, and if the operation is carried out under diminished pressure the substance appears at once in glistening leaflets.

It was soon found that the substance, once set free, sublimes at 100° , and cannot be recrystallised from organic solvents without great loss. Its purification was therefore carried out by sublimation under diminished pressure.

Ergotinine (in some cases ergotoxine) was heated in quantities of 0.5 gram at a time in a flask of 5—10 c.c. capacity, which was provided with a neck 25 cm. long and 1 cm. wide. Almost the whole of the bulb could be immersed in a metal-bath at 220 — 240° ; the lower part of the neck, adjoining the bulb, was jacketed with steam, and the flask was evacuated to 2 mm. pressure. By this means the crystalline sublimate collected only on the upper part of the neck, above the steam-jacket. It was contaminated with a little yellow oil, and was purified as follows. The region of the tube where the sublimate had condensed was cut off, placed in a test-tube, and the substance re-sublimed in a boiling water-bath under a pressure of 15 to 20 mm.; it condensed on the upper portion of the test-tube, from which it was removed by means of a glass rod. In this way 0.09 gram of pure sublimate was obtained from the base from 3 grams of somewhat impure ergotoxine phosphate; in another experiment, 0.5 gram of pure ergotinine yielded 0.021 gram of sublimate, or 4.2 per cent.

As thus obtained, the substance formed thin, large, glistening leaflets, melting in a sealed tube at 109° , readily soluble in cold alcohol, but only sparingly so in cold water and in benzene:

0.0467 gave 0.0881 CO_2 and 0.0325 H_2O . $\text{C}=51.1$; $\text{H}=7.4$.

0.1034 „ 0.1946 CO_2 „ 0.0756 H_2O . $\text{C}=51.3$; $\text{H}=8.1$.

0.0860 „ 8.8 c.c. N_2 (moist) at 19° and 767 mm. $\text{N}=12.0$.

$\text{C}_5\text{H}_9\text{O}_2\text{N}$ requires $\text{C}=52.1$; $\text{H}=7.8$; $\text{N}=12.2$ per cent.

The vapour-density was determined by Victor Meyer's method:

0.0913 gave 22.05 c.c. moist air at 17° and 762 mm. V.D.=53.

$\text{C}_5\text{H}_9\text{O}_2\text{N}=115$ requires V.D.=57.5.

Although the percentage of carbon found is rather low, the formula $\text{C}_5\text{H}_9\text{O}_2\text{N}$ is established with certainty. At first we found

several per cent. too much nitrogen, until we employed cuprous chloride (compare Haas, Trans., 1906, **89**, 570). The same difficulty was experienced by Barger and Carr in determining the nitrogen in ergotinine (Trans., 1907, **91**, 343, footnote), and is apparently due to the presence of a *gem*-dimethyl group, resulting in the formation of methane. We have now actually located this dimethyl group in *isobutyrylformamide*, where, on analysis by Dumas's method, unless cuprous chloride or lead chromate is used, it produces a much larger error than when accompanied by the rest of the molecule in ergotinine. Some of this methane probably also escaped combustion in the carbon and hydrogen estimations quoted.

The melting point of our substance corresponded closely with three substances of the formula $C_5H_9O_2N$ described in the literature, namely, butyrylformamide, *isobutyrylformamide*, and lævulinamide.

We first prepared butyrylformamide by the method given below. This substance was found to have a striking resemblance to the sublimate from the ergot alkaloids, and melted at 108° , but on mixing with this substance the melting point was $89\text{--}90^\circ$. We next prepared *isobutyrylformamide*, which again was quite similar in its properties. It melted at $107\text{--}108^\circ$, and this time the melting point remained unchanged, when the synthetic was mixed with the natural substance. The melting points may be tabulated thus:

1. Butyrylformamide, 108° . Mixture of 1 and 2, $88\text{--}89^\circ$.
2. *iso*Butyrylformamide, $107\text{--}108^\circ$. Mixture of 1 and 3, $89\text{--}90^\circ$.
3. Substance from ergot alkaloids, 109° . Mixture of 2 and 3, $107\text{--}108^\circ$.

In addition, the vapours of 2 and 3 readily gave, on gentle warming, the pyrrole reaction with a pinewood splint moistened with hydrochloric acid, but 1 gave only a doubtful coloration on strongly heating.

The sublimate from the ergot alkaloids is therefore *isobutyrylformamide*, $CHMe_2 \cdot CO \cdot CO \cdot NH_2$.

In addition to this substance we obtained, on destructive distillation of the alkaloids under 2 mm. pressure, a small quantity of a base boiling at $88\text{--}89^\circ$, which was condensed in a tube cooled by carbon dioxide and acetone, and had an odour like pyrrolidine. The substance left in the flask was somewhat volatile under 2 mm. pressure, and crept up the sides of the flask as an amber-coloured, viscid liquid, but could not be distilled.

Synthesis of Butyryl and isoButyrylformamide.

Moritz (Trans., 1881, **39**, 14) prepared butyryl and *isobutyryl*-cyanide from the corresponding chlorides and silver cyanide. We found the yield to be very unsatisfactory, and therefore adopted Claisen's method (*Ber.*, 1898, **31**, 1023), using anhydrous hydrogen

cyanide. 12.5 Grams of butyryl chloride were added to a solution of 3.2 grams of hydrogen cyanide in 46 c.c. of dry ether, and to the well-cooled solution 10 c.c. of pyridine were slowly added. After standing overnight, the pyridine hydrochloride, which had separated, was removed by filtration. The ethereal filtrate was washed with 5 per cent. sulphuric acid to remove the pyridine, and then with water to remove the acid. After drying, the ethereal solution was evaporated, and the residue distilled, when 1 gram of butyrylcyanide was obtained; the rest of the reaction product consisted mostly of the bimolecular polymeride. By hydrolysis with 85 per cent. sulphuric acid, 0.4 gram of butyrylformamide was obtained. It was purified by sublimation from a boiling-water bath under diminished pressure, and melted in a sealed tube at 108° (Moritz found $105-106^{\circ}$). *iso*Butyrylformamide was prepared in the same way, and melted at $107-108^{\circ}$. As stated above, this substance, unlike the normal amide, on heating, readily gives the pyrrole reaction with pinewood. Its melting point is given by Moritz (erroneously) as $125-126^{\circ}$, by Brunner (*Monatsh.*, 1894, 15, 758) as $106-107^{\circ}$, and by Fränke and Kohn (*Monatsh.*, 1899, 20, 887) as 110° .

We desire to acknowledge our indebtedness to Messrs. E. T. Thompson and S. M. Pettet, who have respectively made the microphotographs and drawings, from which the figures of crystals have been prepared.

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XXXI.—*The Action of Chlorine on Phenylcarbamide.*

By FREDERICK DANIEL CHATTAWAY and NEWCOMB KINNEY CHANEY.

THE action of chlorine on phenylcarbamide is of necessity a complicated one, since each of the three hydrogen atoms attached to nitrogen in the compound can be exchanged for halogen, which can also pass into the nucleus by intramolecular rearrangement when the hydrogen of the imino-group connecting the carbonyl and phenyl groups is replaced.

The isolation of the various compounds produced is rendered difficult and in some cases impracticable by the circumstance that the group $\cdot\text{CO}\cdot\text{NHCl}$, which is comparatively stable in presence of hydrochloric acid, at once breaks down with liberation of nitrogen in

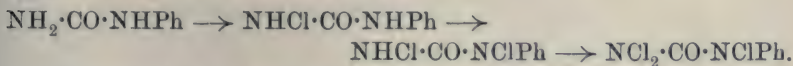
presence of alkali carbonates, whilst the group $\cdot\text{CO}\cdot\text{NCl}\cdot\text{C}_6\text{H}_5$, which is comparatively stable in presence of the latter, undergoes isomeric change under the influence of hydrochloric acid.

Hence, since chlorination has to be effected in acid solution, derivatives containing the unsubstituted phenyl residue, although undoubtedly formed, have not been isolated in a pure state; indeed, only when the phenyl group contains chlorine in all available positions can any considerable number of the *N*-halogen compounds theoretically possible be obtained.

The action of chlorine on phenylcarbamide is interesting, as the halogen passes with great ease at the ordinary temperature, not only into the para- but into both ortho-positions, whilst with acyl anilides the final transformation, in which the halogen enters the second ortho-position, is only effected with some difficulty at a comparatively high temperature.

The *N*-halogen derivatives obtained are also of more than ordinary interest on account of their unexpectedly great stability, for example, 2:4:6-trichlorophenyltrichlorocarbamide can be heated to a temperature approaching 130° without decomposition.

A consideration of the properties of the *N*-chloro-derivatives obtained leads to the conclusion that chlorine enters preferably the amino-group, the hydrogen of the $\cdot\text{NH}\cdot\text{C}_6\text{H}_5$ group being next replaced thus:



The entrance of halogen into the nucleus follows the regular course the para- and ortho-positions being taken up, until finally all three are occupied by halogen.

EXPERIMENTAL.

Action of Chlorine and of Hypochlorous Acid on Phenylcarbamide.

The *N*-chloro-derivatives derivable from unsubstituted phenylcarbamide are undoubtedly formed when chlorine is passed into a solution of phenylcarbamide in glacial acetic acid containing an excess of sodium acetate, but halogen enters the phenyl group with such readiness that they have not been isolated. The considerable evolution of heat which takes place in this action is caused by the entrance of halogen into the ring, since only a very slight development of heat is caused by the replacement of hydrogen in carbamide by halogen.

If to a strongly-cooled solution of phenylcarbamide in alcohol the calculated quantity of *N*/10 aqueous hypochlorous acid is added, a *N*-chloro-derivative separates in the form of a somewhat viscid solid. This dissolves easily in chloroform, and is left on evaporation of the

solvent as a slightly brown, viscid mass, which, without doubt, consists mainly of the compound $\text{NCl}_2 \cdot \text{CO} \cdot \text{NClPh}$, as it contains almost the theoretical amount of chlorine attached to nitrogen and is transformed into a mixture of substituted phenylcarbamides on keeping a solution in glacial acetic acid for some hours. We have not, however, succeeded in bringing it into a crystalline condition. Substituted *N*-chloro-derivatives, although crystallising well from chloroform or petroleum when perfectly pure, can only with great difficulty be made to crystallise when they contain even slight amounts of impurity, especially when, as in the case of those containing unsubstituted phenyl groups, they are of low melting point.

A similar result was obtained when phenylcarbamide suspended in water was chlorinated in presence of excess of calcium carbonate.

p-Chlorophenylchlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound can be prepared by the careful chlorination of phenylcarbamide or of *p*-chlorophenylcarbamide dissolved in glacial acetic acid in presence of excess of sodium acetate. Five grams of *p*-chlorophenylcarbamide were dissolved in 250 grams of glacial acetic acid, and finely powdered, crystalline sodium acetate was added so long as it was dissolved. This liquid was cooled in ice to as low a temperature as possible without crystallisation of the glacial acetic acid, and a slow stream of chlorine passed in. *p*-Chlorophenylchlorocarbamide separated in small, colourless needles. The stream of chlorine was stopped before the whole of the *p*-chlorophenylcarbamide had been converted into the *N*-chloro-derivative, and the latter was collected, washed well with water and finally with chloroform, and dried in a vacuum over phosphoric oxide. It crystallises from warm chloroform, in which it is sparingly soluble, in colourless, fine needles. When heated it remains apparently quite unchanged until 122° , when it suddenly decomposes without previously melting. When treated with hydriodic acid, iodine is quantitatively liberated, and *p*-chlorophenylcarbamide, identical with that obtained from potassium cyanate and *p*-chloroaniline, is formed.

It and the other *N*-chloro-derivatives described in this paper were analysed by the method generally applicable to nitrogen chlorides, by adding known quantities to solutions of potassium iodide containing glacial acetic acid and titrating the iodine liberated with *N*/10-sodium thiosulphate :

0.1083 liberated iodine = 10.4 c.c. *N*/10 I. Cl as : NCl = 17.02.

$\text{C}_7\text{H}_6\text{ON}_2\text{Cl}_2$ requires Cl as : NCl = 17.29 per cent.

p-Chlorophenyldichlorocarbamide, $\text{NCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound separates as a pale yellow solid when the calculated amount of an aqueous solution of hypochlorous acid is rapidly added to a solution of phenylcarbamide in glacial acetic acid. It crystallises from warm acetic acid, in which it is readily soluble, in pale yellow needles, which soften at about 85° and melt and decompose at about 90° :

0.1804 liberated iodine = 30.3 c.c. *N*/10 I. Cl as $\text{:NCl} = 29.77$.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_3$ requires Cl as $\text{:NCl} = 29.6$ per cent.

The yellow colour of the compound indicates that in it two chlorine atoms are attached to the same nitrogen atom.

p-Chlorophenyltrichlorocarbamide, $\text{NCl}_2 \cdot \text{CO} \cdot \text{NCl} \cdot \text{C}_6\text{H}_4\text{Cl}$.

This compound is formed when chlorine in excess is passed into a cooled solution of *p*-chlorophenylcarbamide in glacial acetic acid in presence of excess of sodium acetate. The insoluble *N*-monochloro-derivative first formed slowly dissolves as the passage of the chlorine is continued, and the *N*-trichloro-derivative is obtained as a pale yellow, viscid liquid by diluting with water, extracting with chloroform, and removing the solvent in a current of dry air.

This liquid always gave on analysis a somewhat too low percentage of chlorine as :NCl , and it has never been brought into a crystalline condition. This is probably due to it never having been obtained perfectly pure, but always mixed with a small amount of the corresponding *N*-trichloro-derivative of 2:4-dichlorophenylcarbamide, the passage of the chlorine having to be continued so long to effect the solution of the *N*-monochloro-derivative that transfer of chlorine into the phenyl group in the ortho-position always takes place to a small extent.

2:4-Dichlorophenylmonochlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

This compound is formed when equivalent amounts of 2:4-dichlorophenylcarbamide and of its *N*-dichloro-derivative are dissolved in as small a quantity as possible of warm glacial acetic acid. On cooling, 2:4-dichlorophenylmonochlorocarbamide separates in needle-shaped crystals. It crystallises from hot chloroform, in which it is sparingly soluble, in long, colourless, silky needles. When heated it decomposes at 132° , giving off bubbles of gas and fusing to a brown mass:

0.2215 liberated iodine = 18.7 c.c. *N*/10 I. Cl as $\text{:NCl} = 14.96$.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_3$ requires Cl as $\text{:NCl} = 14.8$ per cent.

2 : 4-Dichlorophenyldichlorocarbamide, $\text{NCl}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

2 : 4-Dichlorophenyldichlorocarbamide can be prepared either from phenylcarbamide or from *p*-chlorophenylcarbamide, and as it is easily soluble in chloroform and crystallises well, it can be separated without difficulty from any small admixture of other products which may be formed together with it.

It is most readily prepared by dissolving phenylcarbamide in from twelve to fifteen times its weight of glacial acetic acid, adding two equivalents of powdered sodium acetate, and passing chlorine until the liquid is saturated. The liquid should be cooled as far as possible during the passage of the gas so that it never becomes even slightly warm. After filtering off, if necessary, a small quantity of 2 : 4 : 6-trichlorophenylmonochlorocarbamide, which is occasionally formed if the chlorination has been continued too long, cooled chlorine-water is added in excess, when the *N*-dichloro-derivative separates as a yellow solid or as a yellow liquid which quickly crystallises. To obtain it dry and free from adhering acid, it is best to add sufficient chloroform to dissolve it, shaking vigorously, then, after washing repeatedly with chlorine-water, separating, and drying the chloroform solution over fused calcium chloride, to drive off the solvent in a current of warm dry air. A yellow, crystalline solid separates as the chloroform volatilises, or if crystallisation does not at once take place, this can be brought about by stirring the deep yellowish-coloured oil with a little petroleum of very low boiling point. It can be similarly easily prepared from *p*-chlorophenylcarbamide or 2 : 4-dichlorophenylcarbamide, but as these are somewhat difficult to procure it is best to proceed as described above.

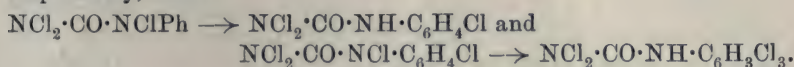
It crystallises well from hot chloroform, in which it is readily soluble, in pale yellow, four-sided, rhombic prisms. It melts at 76° ; when heated above this temperature, it remains apparently unchanged up to 100 — 105° , when it begins to give off gas; the gas evolution is at first very slight, but it increases in amount as the temperature rises until the neighbourhood of 120° is reached, when slight crackling explosions generally occur, due to the evolution and explosion of vapour of nitrogen chloride :

0.3897 liberated iodine = 56.8 c.c. *N*/10 I. Cl as :NCl = 25.84.

$\text{C}_7\text{H}_4\text{ON}_2\text{Cl}_4$ requires Cl as :NCl = 25.88 per cent.

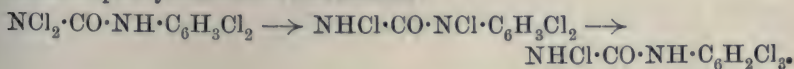
As this compound shows a yellow colour as intense as that of nitrogen chloride, it seems probable that both the chlorine atoms not in the nucleus are attached to the same nitrogen atom, since phenylcarbamide derivatives, which contain only one chlorine atom attached to nitrogen, and the dichloro-derivative of carbamide itself, which

contains two $\cdot\text{NHCl}$ groups, are without appreciable colour. It seems likely that this and the similarly-constituted derivative of *p*-chlorophenylcarbamide are formed by the intramolecular rearrangement of phenyltrichlorocarbamide and *p*-chlorophenyltrichlorocarbamide respectively, thus :



2 : 4-Dichlorophenyl-s-dichlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NCl} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

If 2 : 4-dichlorophenyldichlorocarbamide is dissolved in chloroform and the solvent allowed slowly to evaporate, tufts of slender, colourless prisms are deposited. These can be recrystallised from chloroform, but have never been obtained perfectly pure, as they readily change into 2 : 4 : 6-trichlorophenylmonochlorocarbamide, from which they cannot be completely freed. Different specimens were found to melt not very sharply about $80\text{--}85^\circ$, and to contain amounts of chlorine as NCl varying from about 23.5 to 24.5 per cent., this being from 1 to 2 per cent. too low for the pure substance. Thus the coloured, unsymmetrical *N*-dichloro-derivative when in solution appears slowly to become converted into the colourless, symmetrical derivative, which very easily undergoes transformation into 2 : 4 : 6-trichlorophenylmonochlorocarbamide :



2 : 4 : 6-Trichlorophenylmonochlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_2\text{Cl}_3$.

This, on account of its stability and very sparing solubility in glacial acetic acid, is the most easily prepared of all the *N*-chloro-derivatives of phenylcarbamide. It is formed when either phenylcarbamide, *p*-chlorophenylcarbamide, or 2 : 4-dichlorophenylcarbamide is dissolved in acetic acid and chlorine passed into the liquid for any considerable period. It may be conveniently obtained as follows : Five grams of phenylcarbamide are dissolved in about 25 grams of glacial acetic acid, and a rapid stream of chlorine is passed into the solution, cooling by water so that the temperature does not rise above 20° . After the chlorine has been passing for an hour or thereabouts, fine colourless crystals of 2 : 4 : 6-trichlorophenylmonochlorocarbamide make their appearance in the liquid, and slowly increase in quantity as the passage of the gas is continued. When the separated solid no longer appears to increase in amount, it is collected and washed well with cold glacial acetic acid and afterwards with chloroform. A further quantity of a somewhat impure product can be obtained by adding a little

water to the filtrate. It crystallises from warm glacial acetic acid, in which it is sparingly soluble, in small, very slender, hair-like crystals. When heated it turns brown, and begins to decompose at about 150° , and, if rapidly heated, further melts and decomposes at about 155 — 156° . When dry, it can be kept for a long period at the ordinary temperature without decomposition :

0.2682 liberated iodine = 20.1 c.c. $N/10$ I. Cl as $\text{:NCl} = 13.28$.

$\text{C}_7\text{H}_4\text{ON}_2\text{Cl}_4$ requires Cl as $\text{:NCl} = 12.94$ per cent.

2 : 4 : 6-Trichlorophenylcarbamide, $\text{NH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_2\text{Cl}_3$.

This compound is most easily obtained by replacing the *N*-halogen atom in 2 : 4 : 6-trichlorophenylmonochlorocarbamide by hydrogen.

Five grams of 2 : 4 : 6-trichlorophenylmonochlorocarbamide were suspended in 20 c.c. of glacial acetic acid, and 2 grams of powdered potassium iodide added. The iodine liberated was removed as fast as it was formed by adding an aqueous solution of sodium sulphite. When iodine was no longer liberated, a slight excess of sulphite solution was added, the liquid was warmed for some time on a water-bath, and kept for twenty-four hours. The 2 : 4 : 6-trichlorophenylcarbamide thus formed was then collected and recrystallised from alcohol. It separates from boiling alcohol, in which it is moderately easily soluble, in colourless, long, hair-like crystals. When heated rapidly it melts at 250° , and decomposes and evolves gas at a slightly higher temperature :

0.1422 gave 0.2545 AgCl . Cl = 44.24.

$\text{C}_7\text{H}_5\text{ON}_2\text{Cl}_3$ requires Cl = 44.42 per cent.

2 : 4 : 6-Trichlorophenyldichlorocarbamide, $\text{NHCl} \cdot \text{CO} \cdot \text{NCl} \cdot \text{C}_6\text{H}_2\text{Cl}_3$.

This and the *N*-trichloro-derivative are best obtained from pure 2 : 4 : 6-trichlorophenylcarbamide. Five grams of 2 : 4 : 6-trichlorophenylcarbamide were dissolved in 500 grams of cold glacial acetic acid, and a rapid stream of chlorine passed in for about ten minutes until the chlorine escaped freely. The clear yellow liquid thus produced was diluted with an equal bulk of water and extracted with chloroform. The chloroform solution was thoroughly washed with water, dried over fused calcium chloride, and the solvent driven off by a current of warm dry air. A very pale yellowish-coloured oily liquid was thus obtained, which on stirring with a little light petroleum deposited a white solid in fine granular crystals. This was recrystallised from hot chloroform, in which it is sparingly soluble, and separates in colourless, probably orthorhombic prisms terminated by dome or pyramidal faces. On being heated it remains apparently unchanged up to 128° , when it begins to decompose with crackling explosions without previously

melting. At this point chlorine is evolved, and it seems probable that the explosions are due to the liberation of the vapour of nitrogen chloride, which explodes as soon as it is formed, setting free chlorine :

0.2111 liberated iodine = 27.5 c.c. *N*/10 I. Cl as :NCl = 22.93.

$C_7H_3ON_2Cl_5$ requires Cl as :NCl = 22.99 per cent.

The circumstance that this compound is colourless leads to the conclusion that the two chlorine atoms attached to nitrogen are not attached to the same nitrogen atom, as does also its relatively high melting point.

2 : 4 : 6-*Trichlorophenyltrichlorocarbamide*, $NCl_2 \cdot CO \cdot NCl \cdot C_6H_2Cl_3$.

Four grams of 2 : 4 : 6-trichlorophenylcarbamide were mixed with about 8 grams of finely powdered sodium acetate and suspended in 50 grams of glacial acetic acid. The liquid was kept cool, and a slow stream of chlorine was passed in for an hour. The solution was then filtered, diluted with chlorine water, and extracted with chloroform. The chloroform extract was then repeatedly shaken with a cooled solution of chlorine water containing a little sodium acetate. On separating, drying with fused calcium chloride, and driving off the chloroform in a current of warm dry air, a deep yellowish-coloured, viscid liquid was obtained. On dissolving this in warm petroleum of low boiling point and keeping the solution for some hours, 2 : 4 : 6-trichlorophenyltrichlorocarbamide separated in bright yellow, short, glistening prisms.

It melts at 58° , and can be heated to 130° without apparent change. When heated above this temperature, bubbles of gas are liberated, and in the neighbourhood of 155° it darkens and completely decomposes :

0.2209 liberated iodine = 38.55 c.c. *N*/10 I. Cl as :NCl = 30.90.

$C_7H_2ON_2Cl_6$ requires Cl as :NCl = 31.02 per cent.

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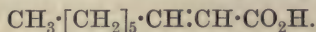
XXXII.— Δ^1 -Nonylenic Acid.

By VICTOR JOHN HARDING and CHARLES WEIZMANN.

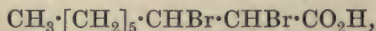
IN the present communication an account is given of the preparation in large quantities and the means of identification of Δ^1 -nonylenic acid, an acid of considerable technical importance. It was first obtained by Schneegans (*Annalen*, 1885, **227**, 80), who prepared it by the condensation of heptaldehyde and sodium

acetate by means of acetic anhydride at 160—170° for thirty hours. The yield was very poor, and its identification uncertain. Knoevenagel (Friedländer: *Fortschritte der Teerfarbenfabrikation*, 7, 738) has also prepared this acid by the condensation of heptaldehyde and malonic acid through the agency of piperidine. The authors, however, have not been able to obtain large yields by this method, the piperidine inducing condensation products of heptaldehyde with itself similar in character to those obtained by means of alkalis. These high-boiling neutral products also occurred when other secondary or primary bases, such as diethylamine, ammonia, or aniline, were used as the condensing agent, and it was only when tertiary bases were employed that good yields of the desired acid were obtained. The heptylidenemalonic acid which is first obtained,

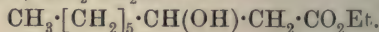
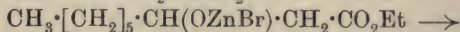
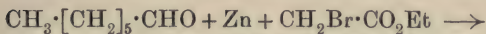
$\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CHO} + \text{CH}_2(\text{CO}_2\text{H})_2 = \text{H}_2\text{O} + \text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH} : \text{C}(\text{CO}_2\text{H})_2$,
easily loses carbon dioxide to form Δ^1 -nonylenic acid,



This unsaturated acid, after purification by means of its barium salt, boils at 144°/13 mm., and is obtained as a colourless oil with a characteristic odour. As a means of identification, the authors recommend the use of the amide or the *p*-toluidide, but more especially the former, as its preparation in a pure state is both easy and rapid. Δ^1 -Nonylenamide melts at 126—127°; the *p*-toluidide at 73—74°. The dibromo-acid,



although it has been obtained as a solid melting at 35°, on account of the difficulty with which it is prepared, is not suitable as a means of identification. Δ^1 -Nonylenic acid, on reduction with sodium and alcohol, gives nonyl alcohol. In order to control the constitution of the unsaturated acid, an alternative method of preparation was adopted. This was the condensation of heptaldehyde and ethyl bromoacetate by means of zinc:



Ethyl β -hydroxy-*n*-nonoate, on hydrolysis, gives the corresponding acid as a white, crystalline solid, melting at 57—59°. This acid has previously been prepared by Wagner (*Ber.*, 1894, **27**, 2736), who obtained it by the oxidation of hexylallylcarbinol by means of permanganate. Wagner gives the melting point of this acid as 48—51°, but we do not think there can be any doubt as to the identity of the two substances. The removal of water from the hydroxy-acid was accomplished by means of acetic anhydride, a

method which has been used with such conspicuous success by Wallach to produce unsaturated acids containing the ethylene linking in the $\alpha\beta$ -position. The identity of the two preparations of Δ^1 -nonylenic acid was proved by means of their amides, a mixture of the two preparations having the same melting point as their separate constituents.

EXPERIMENTAL.

Δ^1 -Nonylenic Acid, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$.

After many unsuccessful attempts, the following method of preparing Δ^1 -nonylenic acid was found to give the best results. One hundred grams of malonic acid were dissolved in 160 grams of pyridine, and to the cold liquid was added 100 grams of heptaldehyde. The whole was kept at the ordinary temperature for thirty-six hours, and then gently heated on the water-bath for two hours. The product was poured into water, and acidified with hydrochloric acid. The oil was extracted by ether, and well washed with water. The unsaturated acid was next removed from the ethereal extract by means of sodium carbonate solution. The ethereal solution was dried and evaporated, when the very small residue which was obtained was found to consist almost entirely of unchanged heptaldehyde, high condensation products being produced only in very small amount. The sodium carbonate washings, on acidification, extraction with ether, drying, and distillation, yielded 90 grams of Δ^1 -nonylenic acid, boiling at $145\text{--}150^\circ/12\text{ mm.}$ Analyses of this acid, even on redistillation, always showed a deficiency of carbon, and several methods of purification were tried, of which the following gave the best results. Eighty grams of the distilled acid were boiled in 95 per cent. alcohol with 127 grams of pure barium hydroxide. The barium salt which is formed gradually dissolves in much boiling alcohol, from which it separates on cooling as a white, crystalline powder. This, on acidifying with dilute hydrochloric acid and extraction with ether, gave about 40 grams of pure Δ^1 -nonylenic acid, boiling constantly at $144^\circ/13\text{ mm.}$:

0.1210 gave 0.3097 CO_2 and 0.1102 H_2O . $\text{C}=69.7$; $\text{H}=10.1$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

Δ^1 -Nonylenic acid is a colourless oil, with the faint odour characteristic of acids of this class. It is readily soluble in cold sodium carbonate solution, and instantly decolorises cold alkaline permanganate. The preparation of Δ^1 -nonylenic acid in good yield was also attempted by condensing heptaldehyde and malonic acid by the use of piperidine (Knöevenagel, *loc. cit.*), but the yields were

very poor, large amounts of high-boiling condensation products of heptaldehyde with itself being formed. This is easily shown if to heptaldehyde alone a few drops of piperidine are added. The liquid rapidly becomes hot, loses the characteristic odour of heptaldehyde, and decomposes on distillation. Similar results are given by other primary and secondary bases, such as ammonia, aniline, and diethylamine. The condensation of heptaldehyde and malonic acid by means of dimethylaniline gave, from 100 grams of heptaldehyde, 30 grams of Δ^1 -nonylenic acid and also some condensation products of high boiling point. These we attribute to the presence of methylaniline in the dimethylaniline employed.

Δ^1 -Nonylenyl Chloride.—Nonylenic acid reacts vigorously with phosphorus pentachloride to form Δ^1 -nonylenyl chloride, boiling at $144^\circ/90$ mm.: *

0.2861 gave 0.2335 AgCl. Cl=19.9.

$C_9H_{15}OCl$ requires C=20.1 per cent.

The *methyl* and *ethyl* esters boil respectively at $110^\circ/20$ mm. and $123^\circ/25$ mm.

Δ^1 -Nonylenamide, $C_8H_{15}\cdot CO\cdot NH_2$.—This most characteristic derivative of Δ^1 -nonylenic acid is very readily prepared by pouring the acid chloride into concentrated aqueous ammonia. The amide instantly separates as a solid, and is collected and purified by crystallisation from aqueous methyl alcohol or petroleum. It crystallises in beautiful pearly leaflets, melting at 126 — 127° :

0.1741 gave 13.9 c.c. N_2 (moist) at 20° and 752 mm. N=9.0.

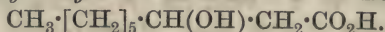
$C_9H_{17}ON$ requires N=8.9 per cent.

*Δ^1 -Nonyleno-*p*-toluidide* is prepared by adding the acid chloride to a slight excess of *p*-toluidine and then gently warming. The yellow, semi-solid mass which is produced is then treated several times with dilute hydrochloric acid and with sodium carbonate solution. The adhering oil is removed by contact with porous porcelain, and leaves the *p*-toluidide as a white solid, which crystallises from light petroleum in small, shining leaflets melting at 73 — 74° :

0.1610 gave 7.6 c.c. N_2 (moist) at 19° and 770 mm. N=5.5.

$C_{16}H_{23}ON$ requires N=5.7 per cent.

β -Hydroxy-n-nonoic Acid and its Ester,



This acid is easily and rapidly prepared by condensing heptaldehyde and ethyl bromoacetate by means of zinc in benzene solution. Eighty-eight grams of heptaldehyde and 128 grams of ethyl bromoacetate are mixed with twice their volume of benzene,

and 52 grams of zinc added. The reaction is started by warming on the water-bath, but when once commenced is extremely vigorous, and cooling must be resorted to. When the reaction has subsided, the condensation may be completed by heating on the water-bath for a couple of hours. The viscous product is decomposed by ice and hydrochloric acid, extracted with ether, the ethereal extract well washed with water, dried, and distilled, when ethyl β -hydroxy-*n*-nonoate passes over as a colourless, inodorous oil, boiling at $145^\circ/13$ mm.:

0.1381 gave 0.3302 CO_2 and 0.1287 H_2O . $\text{C}=65.2$; $\text{H}=10.4$.

$\text{C}_{11}\text{H}_{22}\text{O}_3$ requires $\text{C}=65.3$; $\text{H}=10.8$ per cent.

When treated with an aqueous solution of hydrogen bromide saturated at 0° , this hydroxy-ester only gives very small quantities of ethyl β -bromo-*n*-nonoate, the hydroxy-group remaining unaffected. β -Hydroxy-*n*-nonoic acid is easily obtained by the hydrolysis of its ester by means of alcoholic potash. The potassium salt, which separates in large plates from the alcoholic solution on cooling, is collected, dissolved in a little water, cooled with ice, and acidified, when β -hydroxy-*n*-nonoic acid separates as an oil which rapidly solidifies. This is collected, any adhering oil being removed by contact with porous porcelain, and purified by crystallisation from hot water, or from light petroleum, when it melts at $57\text{--}59^\circ$:

0.1193 gave 0.2707 CO_2 and 0.1102 H_2O . $\text{C}=61.9$; $\text{H}=10.2$.

$\text{C}_9\text{H}_{18}\text{O}_3$ requires $\text{C}=62.1$; $\text{H}=10.3$ per cent.

β -Hydroxy-*n*-nonoic acid crystallises in short needles as a white, inodorous compound. It is readily soluble in cold benzene, alcohol, chloroform, acetic acid, or ethyl acetate, and is stable towards cold alkaline permanganate. It is instantly soluble in cold sodium carbonate solution. When treated with an acetic acid solution of hydrogen bromide and gently warmed, it yields β -bromo-*n*-nonoic acid as a heavy oil.

*Preparation of Δ^1 -Nonylenic Acid from β -Hydroxy-*n*-nonoic Acid.*

In order to confirm the constitution of Δ^1 -nonylenic acid prepared from heptaldehyde and malonic acid, it was deemed advisable to prepare it from β -hydroxy-*n*-nonoic acid, using acetic anhydride as a dehydrating agent. Ten grams of crude β -hydroxy-*n*-nonoic acid were boiled with 50 c.c. of acetic anhydride for four hours. The product was poured into water, and distilled in a current of steam, when the unsaturated acid passed over slowly. The distillate was saturated with ammonium sulphate, extracted with ether, and frac-

tionated under diminished pressure, when the acid (5 grams) was found to boil at $181^\circ/60$ mm.:

0.1315 gave 0.3293 CO_2 and 0.1237 H_2O . $\text{C}=68.3$; $\text{H}=10.4$.

$\text{C}_9\text{H}_{16}\text{O}_2$ requires $\text{C}=69.2$; $\text{H}=10.2$ per cent.

The acid prepared in this way possessed a sharper odour than that prepared by the first method, but its identity was proved beyond all doubt by its conversion into the acid chloride and then into the amide. The amide, when crystallised from petroleum, melted at 126° , and when mixed with a specimen of Δ^1 -nonylenamide prepared from malonic acid, no alteration in the melting point was observed.

Reduction of Ethyl Δ^1 -Nonylenate to Nonyl Alcohol.

Fifty grams of ethyl nonylenate, prepared from the crude acid, are dissolved in 150 grams of absolute alcohol, and gradually added to 50 grams of sodium contained in a large flask provided with a reflux condenser, the temperature being kept at 150° . The reduction is very vigorous, and alcohol must be added from time to time to complete the solution of the sodium. When all the sodium has dissolved, the product is distilled in a current of steam, the nonyl alcohol being extracted by ether and fractionated. The yield is 35 per cent. The nonyl alcohol was identified by means of its phenylurethane.

$\alpha\beta$ -Dibromo-n-nonoic Acid, $\text{CH}_3\cdot[\text{CH}_2]_5\cdot\text{CHBr}\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$.

This acid is prepared by the addition of bromine to a solution of Δ^1 -nonylenic acid in carbon disulphide until the bromine ceases to be decolorised. The carbon disulphide is distilled off, the acid dissolved in ether, washed with dilute sulphurous acid, dried, and the ether evaporated. After a long time in an evacuated desiccator, the yellow oil gradually solidifies to a white, crystalline solid. This is pressed on porous porcelain to remove adhering oil, but the acid is too soluble in all organic solvents to permit of a convenient crystallisation. It melts at 35° :

0.2125 gave 0.2450 AgBr . $\text{Br}=49.1$.

$\text{C}_9\text{H}_{16}\text{O}_2\text{Br}_2$ requires $\text{Br}=50.6$ per cent.

It is soluble in dilute sodium carbonate solution, but the solution rapidly becomes cloudy, owing to the separation of α -bromo- Δ^1 -nonylenic acid.

XXXIII.—*Strychnine, Berberine, and Allied Alkaloids*

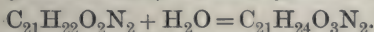
By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

I.—*Strychnine and Brucine.*

SEVERAL years ago (Trans., 1889, 55, 63; 1890, 57, 992) one of us carried out a systematic study of the alkaloid berberine, and succeeded in obtaining a series of degradation products, the investigation of which made it possible to suggest a constitutional formula for berberine, and this formula, except for slight modifications in minor details, is still accepted as correct. The intention at that time was to use the experience obtained in order to attack the problem of the constitutions of several other alkaloids, and afterwards to attempt their synthesis, and a series of experiments on cryptopine* (Proc., 1891, 7, 166) and on other opium alkaloids were commenced.

Owing, however, to the necessity for completing other investigations, these researches had, for the time, to be reluctantly put aside.

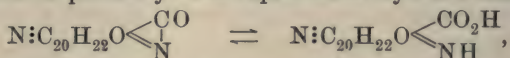
In recent years the difficult problem of the constitution of brazilin and hæmatoxylin made it imperative that we should very carefully study the constitution and nature of the groupings contained in natural products generally, and particularly in the alkaloids, and, in reviewing the work which had been published on strychnine, brucine, berberine, corydaline, and allied alkaloids, we were led to certain conclusions as to their constitutions which we think may be worth recording, and the validity of which we propose to test by experiment. Although the alkaloids, strychnine and brucine, have been the subject of detailed investigations, especially at the hands of Tafel and Leuchs, very few deductions have been made as to their constitutions. It is well known that strychnine, $C_{21}H_{22}O_2N_2$, while containing two atoms of nitrogen, is only a mon-acid base, yielding salts, such as the hydrochloride, $C_{21}H_{22}O_2N_2 \cdot HCl + 1\frac{1}{2}H_2O$, with only one equivalent of the acid. It is also known that the alkaloid is a tertiary base, and that it does not contain methoxy-groups. When strychnine is treated with alkalis (Loebisch and Schoop, *Monatsh.*, 1886, 7, 75; Tafel, *Annalen*, 1891, 264, 49), it suffers hydrolysis with the addition of a molecule of water and formation of strychnic acid (and *isostrychnic acid*, p. 317):



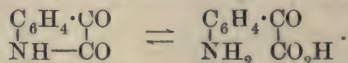
Strychnic acid is an imino-carboxylic acid, and at the same time

* Owing to the generosity of Messrs. T. and H. Smith, of Edinburgh, who have supplied me with considerable quantities of this very rare alkaloid, this investigation is being continued.—W.H.P., jun.

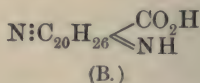
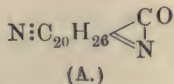
a tertiary base, since it yields metallic salts and, when treated with methyl iodide, is converted into methylstrychnic acid methiodide, $C_{20}H_{22}ON(MeI)(:NMe) \cdot CO_2H$ (Tafel, *Annalen*, 1891, **264**, 59), and the presence of the imino-group is further demonstrated by the formation of a nitrosamine, $C_{20}H_{22}ON(:N \cdot NO) \cdot CO_2H$, when the acid is treated with nitrous acid. These results, together with the fact that strychnic acid is readily converted into strychnine by heat, led Tafel to suggest that the relationship of strychnine to strychnic acid is probably that represented by the scheme:



and is similar to that existing between ψ -isatin and isatinic acid:

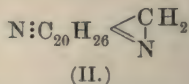
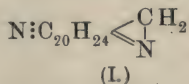


It can scarcely be doubted that this representation is correct, and the non-basic properties of the grouping $\cdot CO \cdot N:$ affords an explanation of the fact that strychnine, although it contains two nitrogen atoms, is only capable of combining with one equivalent of an acid. Further confirmation of the presence of the grouping $\cdot CO \cdot N:$ in strychnine is obtained from the study of the products which are formed when the alkaloid is treated with various reducing agents. When strychnine is reduced with phosphorus and hydriodic acid, it is converted into a substance, $C_{21}H_{26}ON_2$, called desoxystrychnine (Tafel, *Annalen*, 1892, **268**, 245), and this substance, the importance of which is emphasised in the following pages, evidently has the formula (A):



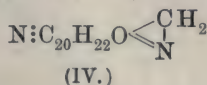
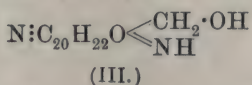
since, like strychnine itself, it is a mon-acid base, which, on hydrolysis, yields desoxystrychnic acid (B).

This imino-acid has properties very similar to those of strychnic acid, and its whole behaviour indicates that the characteristic groups $N:$ and $\cdot CO \cdot N:$ of strychnine have undergone no change during the reduction to desoxystrychnine. When desoxystrychnine is treated with sodium and alcohol, it yields strychnoline (I), the $\cdot CO \cdot N:$ group becoming $\cdot CH_2 \cdot N:$, but electrolytic reduction proceeds further and causes the addition of another two atoms of hydrogen, and dihydrostrychnoline (II) results (Tafel, *Annalen*, 1898, **301**, 324 and 326):



Lastly, when strychnine itself is reduced electrolytically, it yields

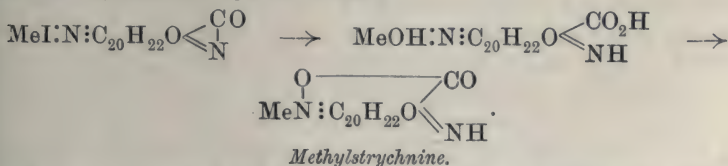
tetrahydrostrychnine (III), the group $\cdot\text{CO}\cdot\text{N}\cdot$ being reduced to $\cdot\text{CH}_2(\text{OH})\text{NH}\cdot$, and this readily loses water with formation of strychnidine (IV) (Tafel, *Annalen*, 1898, **301**, 303):



One of the most characteristic properties of strychnine is the ease with which it is nitrated, since warming with very dilute nitric acid (5 per cent.) converts it into dinitrostrychnine hydrate, $\text{C}_{21}\text{H}_{22}\text{O}_3\text{N}_2(\text{NO}_2)_2\cdot\text{H}_2\text{O}$ (Tafel, *Annalen*, 1898, **301**, 299).

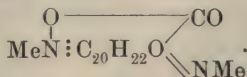
This behaviour, and also the fact that strychnine is very readily sulphonated (Leuchs and Schneider, *Ber.*, 1909, **42**, 2681), may be taken as proof of the presence of at least one benzene ring, and it will be shown later that all the evidence points to there being only one such ring in the molecule. There can, furthermore, be little doubt that this benzene ring forms part of a quinoline nucleus, and, although no known quinoline derivative has so far been obtained from strychnine, there is ample indirect evidence of the presence of such a nucleus.

Tafel (*Annalen*, 1898, **301**, 336) investigated the action first of dilute and then of strong nitric acid on strychnine, and showed that, under the conditions he employed, the alkaloid is nitrated and suffers degradation with the formation of dinitrostrychnol-carboxylic acid, $(\text{NO}_2)_2\text{C}_9\text{H}_2\text{N}(\text{OH})_2\cdot\text{CO}_2\text{H}$, and this important acid, when heated at 200° , loses carbon dioxide, with the formation of dinitrostrychnol, $(\text{NO}_2)_2\text{C}_9\text{H}_3\text{N}(\text{OH})_2$. There can be little doubt, as, indeed, Tafel has suggested, that this latter substance is a dinitrodihydroxyquinoline, and we are at present engaged in its investigation, not only with the object of proving this point, but also, at the same time, of determining the relative positions of the substituent groups in the quinoline nucleus. Still more conclusive evidence of the presence of the quinoline nucleus in strychnine has been obtained in the following way. Strychnine combines with methyl iodide to yield strychnine methiodide, $\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2\cdot\text{MeI}$, and this, on treatment with silver hydroxide, or barium hydroxide, yields methylstrychnine, and, since this substance shows all the properties of a betaine, there can be little doubt that its formation is to be represented by the scheme:

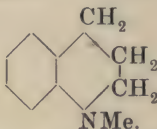


Methylstrychnine has all the properties of a secondary base; it

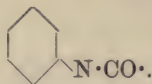
yields, for example, a nitrosamine, and reacts with methyl iodide to form dimethylstrychnine:



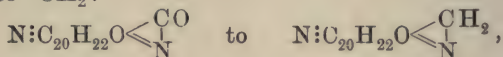
Tafel (*Annalen*, 1891, **264**, 43) has already pointed out how remarkably the properties of dimethylstrychnine resemble those of *N*-methyltetrahydroquinoline:



and dimethylaniline. Like these substances, dimethylstrychnine yields a green nitroso-derivative, and condenses with benzaldehyde in the presence of zinc chloride with the formation of the leuco-base of a green colouring matter, which closely resembles malachite-green and the green colouring matter obtained from *N*-tetrahydroquinoline under the same conditions; furthermore, it combines with diazobenzenesulphonic acid to yield a yellow azo-dye. Because of this behaviour, Tafel draws the conclusion, not only that strychnine contains a quinoline nucleus, but also that the :NMe group in dimethylstrychnine and the :NH group in methylstrychnine, and therefore the :N·CO· group in strychnine, is combined by one linking direct to the benzene ring, and that strychnine must therefore contain the grouping:



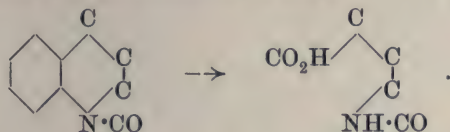
The consideration of the properties of strychnidine leads to exactly the same conclusions. This substance is produced, as explained on p. 307, by the reduction of the CO· group in strychnine to ·CH₂:



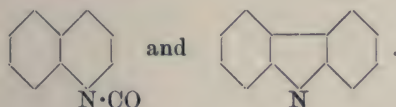
and this process converts a substance with the properties of acetanilide into one which again exhibits exactly the behaviour of dimethylaniline or *N*-methyltetrahydroquinoline towards reagents.

The most valuable evidence as to the internal structure of the other portion of the strychnine molecule is obtained from the consideration of the properties of an important monobasic acid, C₁₅H₁₇O₂N₂·CO₂H, which is produced when strychnine is oxidised by chromic acid (Hanssen, *Ber.*, 1884, **17**, 2849; 1885, **18**, 777 and 1917; 1887, **20**, 451). This acid is also obtained under the same conditions from brucine, an alkaloid which contains two

methoxy-groups and has properties so exactly similar to those of strychnine that there can be no doubt that it is dimethoxy-strychnine. Since the two methoxy-groups disappear during the formation of the acid $C_{15}H_{17}O_2N_2 \cdot CO_2H$ from brucine, it follows that the benzene ring of the quinoline nucleus in the two alkaloids, brucine and strychnine, is broken down during the formation of this acid, evidently in the following manner:



Now the acid $C_{15}H_{17}O_2N_2 \cdot CO_2H$ is a derivative of carbazole, because it yields this substance on distillation with zinc dust, and we therefore arrive at the conclusion that the molecule of strychnine must contain the two residues:

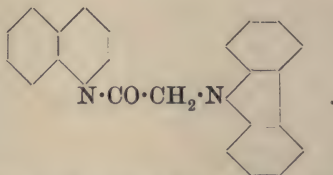


It has already been shown that the quinoline nucleus contains a benzene ring, and therefore, in order to account for the large number of hydrogen atoms in the strychnine molecule, it is necessary, as it appears to us, to conclude that not only the pyridine ring of the quinoline nucleus, but also the carbazole section of the molecule must be almost completely reduced. Adopting a line of argument which we have employed on previous occasions (Trans., 1890, **57**, 1004; 1902, **81**, 238; 1908, **93**, 491), we find that these facts afford a basis on which it is possible to build up constitutional formulæ for strychnine and its derivatives which, we are convinced, must at least be very near the truth.

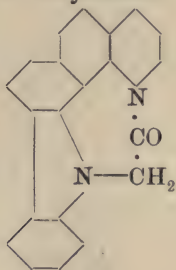
The two residues just figured contain C_{22} , and as the formula of strychnine is $C_{21}H_{22}O_2N_2$, it follows that these two residues must be fused together in such a way that one carbon atom at least is common to both. It is clear that the basic nature of strychnine is not due to the nitrogen atom of the tetrahydroquinoline nucleus, because of its union with the CO group; it must therefore be due to the nitrogen atom of the carbazole residue. If we now attempt to construct a formula for strychnine on the assumption that the two residues are united in such a way that one carbon atom is common to both, we have to remember that strychnine is a tertiary base, and the nitrogen of the reduced carbazole residue must therefore be rendered tertiary by union with a carbon atom of the quinoline nucleus, whilst the CO group unites with the carbazole

nucleus. This would lead to formulæ which clearly cannot represent the skeleton of strychnine.

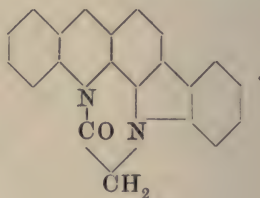
It seems to us that the only possible alternative is to assume that, in the fusion of the two nuclei, two carbon atoms become common to both,* and that the skeleton, which now contains C_{20} , is completed by the introduction of an additional carbon atom between the CO group and the basic nitrogen atom,† yielding, in the first place:



Further fusion may now take place in two ways, and two only, and leads us to the following alternative expressions for the skeleton of strychnine:

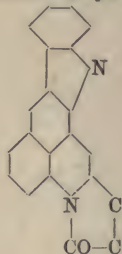


(I.)



(II.)

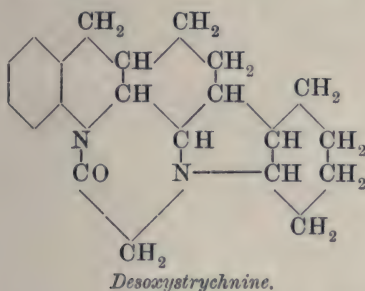
* If the two nuclei are fused together in such a way that three carbon atoms are common to both, then two additional carbon atoms must be introduced, and we obtain expressions such as the following for the skeleton of strychnine:



In such cases the carboxylic group in strychnic acid methiodide would be so far removed from the iodine atom that the formation of a betaine would appear to be out of the question (p. 307).

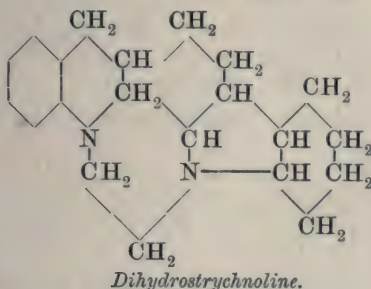
† For, if not, then the only other possible way of uniting the $:N\cdot CO\cdot$ group with the rest of the molecule, in order to make the basic nitrogen atom tertiary, is the construction of a four-carbon ring, which is highly improbable.

Formula I contains a seven-membered ring, and it is very unlikely that such a ring would be readily produced by the elimination of water from strychnic acid; on the other hand, such elimination leading to the formation of a six-membered ring is quite usual, and for this and other reasons we prefer formula II. If this formula be accepted as the skeleton of strychnine, there can be little doubt that desoxystrychnine, $C_{21}H_{26}ON_2$, the product of the reduction of strychnine with phosphorus and hydriodic acid (p. 306), must be written:



and this formula is in complete agreement with the properties of this substance. It exhibits desoxystrychnine as a derivative of tetrahydroquinoline, accounts for its conversion into desoxystrychnic acid, and for the behaviour of this acid, as well as of desoxystrychnine itself, towards methyl iodide, nitrous acid, etc.

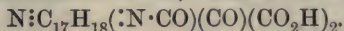
Similarly, the highest product of the hydrogenation of strychnine, namely, dihydrostrychnoline, $C_{21}H_{28}N_2$ (p. 306), will be represented by the formula:



and the fact that further hydrogenation, without reduction of the benzene ring, is impossible is well indicated by this structure.

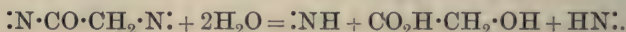
On the basis of skeleton formula II, it is possible not only to explain the recent important results of Leuchs (*Ber.*, 1908, **41**, 1711), Leuchs and Schneider (*ibid.*, 4393; 1909, **42**, 2494), and Leuchs and Weber (*Ber.*, 1909, **42**, 3703), but also to deduce a constitutional formula for strychnine which cannot be very far from the truth.

Leuchs and his collaborators find that strychnine, on oxidation in acetone solution with permanganate, is converted into a keto-dibasic acid, strychninonic acid, which has the composition,



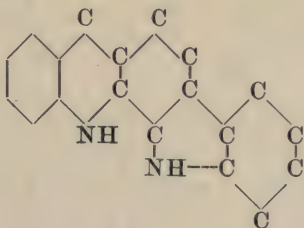
On reduction with sodium amalgam, this acid yields the corresponding secondary alcohol dibasic acid, strychninolic acid, $\text{N}:\text{C}_{17}\text{H}_{18}(\text{:N}\cdot\text{CO})(\text{CH}\cdot\text{OH})(\text{CO}_2\text{H})_2$, and this substance, on treatment with dilute potassium hydroxide, is decomposed, yielding glycollic acid and strychninolone, $\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$, a substance which possesses neither acid nor basic properties. An exactly similar series of products was also obtained from brucine under the same conditions.

There can be no doubt that the formulæ for strychninonic and strychninolic acids suggested by Leuchs, which represent these acids as containing a tertiary nitrogen atom, are correct, and the absence of basic properties is amply explained by the presence of the two carboxyl groups. When strychninolic acid loses glycollic acid under the influence of alkali, the substance produced, strychninolone, is devoid of both acid and basic properties, and it is therefore obvious that, during its formation, mutual neutralisation has taken place between the two carboxyl groups and basic nitrogen atoms. Since two such atoms are required for this process, it follows that the section $\text{:N}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}:$ of the original strychnine skeleton must have lost the grouping $\cdot\text{CO}\cdot\text{CH}_2\cdot$, and this is therefore the source of the glycollic acid:

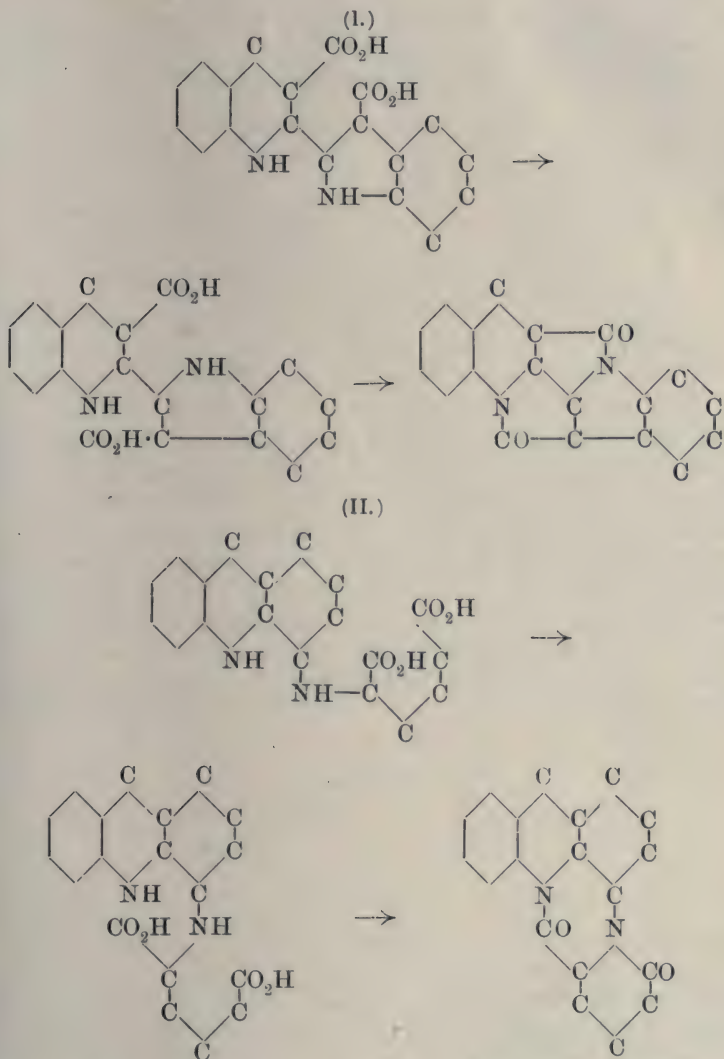


The cause of the non-basic nature of one of the nitrogen atoms in strychnine is thus removed, and the two :NH groups are now both basic and free to combine with two carboxyl groups to yield a neutral substance, such as strychninolone.

The problem which still remains is to discover the process by which the structure:

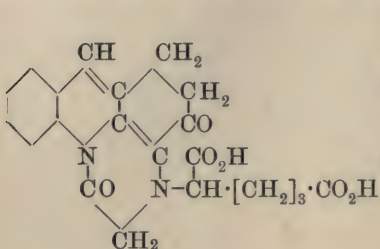


can be broken up in order to supply two carboxyl groups in such positions that they can combine with the two :NH groups to yield two neutral $\text{:N}\cdot\text{CO}\cdot$ groupings. The following appear to be the only two ways in which this can be satisfactorily accomplished:

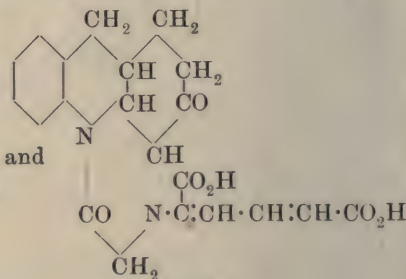


If now the hydrogen atoms and the carboxyl and other groups in strychninonic acid, $N:C_{17}H_{18}(:N \cdot CO)(CO)(CO_2H)_2$, are filled into the first formula of scheme I, it will be found that the complete expression must contain one double linking, whereas, if the same process is carried out in the case of scheme II, two double linkings will be found to be necessary. This difference is due to the fact that, in developing scheme I from the skeleton formula of strychnine, one closed ring suffers fission, whereas in the case of scheme II two closed rings suffer disruption.

If we consider, in the first place, the development of a formula for strychninonic acid on the basis of the first skeleton formula of scheme II, we arrive at expressions of the types :



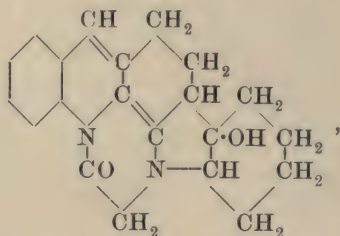
(I.)



(II.)

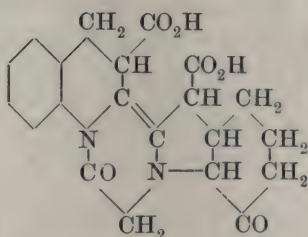
It can be shown in several ways that such formulæ cannot represent strychninonic acid, and the same is true of any other formulæ built up on the basis of the first skeleton formula of scheme II, but only one reason for this need be given here.

Strychninonic acid is obtained from strychnine by a simple permanganate oxidation, and it must therefore be possible to reconstruct the formula of strychnine in a comparatively simple manner from that of strychninonic acid. If we select formula I, and attempt to construct from it a formula for strychnine, we arrive at the expression :

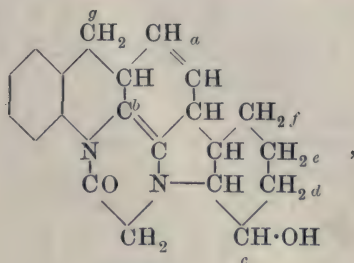


which cannot be correct, because oxidation with permanganate would attack the double linking combined with the benzene ring, and it would therefore be impossible to obtain from this expression the formula for strychninonic acid from which it was derived, and the same line of argument applies equally to all other formulæ derived from the first skeleton formula of scheme II.

Whilst, then, scheme II is out of the question, careful consideration shows that scheme I leads to the following expressions for strychninonic acid and strychnine :

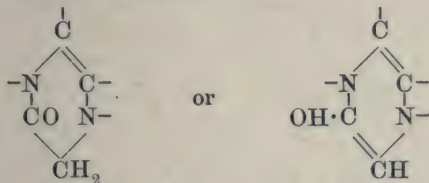


Strychninonic acid.



Strychnine.

which seem to us to be in every way satisfactory, since they account in a comparatively simple manner for all the known reactions of these substances. From the several possibilities we were led to select the positions assigned to the double linkings in the strychnine formula for various reasons, and of these the following need only be discussed. If the formula assigned to strychninonic acid is correct, the formation of this acid by the oxidation of strychnine clearly points to one of the double linkings occupying the position marked *a*. The position *b* was selected for the second double linking, because this linking must be situated in a stable portion of the molecule, otherwise it would also suffer oxidation under the conditions employed in the preparation of strychninonic acid, and experience of heterocyclic systems has shown that the double linkings in nuclei, such as:



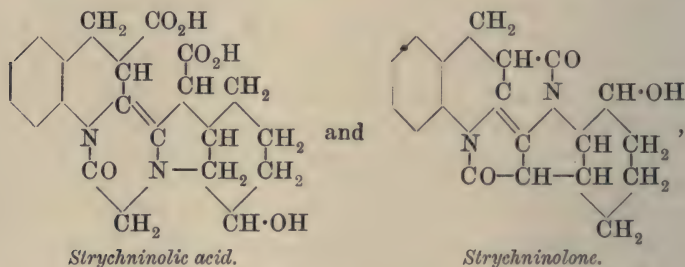
are not readily oxidised. Strychninonic acid is a keto-dibasic acid, and there can be little doubt that the keto-group is produced by the oxidation of a secondary alcohol group; in other words, the molecule of strychnine contains a :CH(OH) group (compare Leuchs, *Ber.*, 1908, **41**, 1711), and the difficult problem remaining to be solved is that of assigning the correct position to this group.

It cannot occupy the position *g*, because this would make strychninonic acid a derivative of benzoylacetic acid, and *f* and *e* seem also to be out of the question, for the reason that hydroxy-groups in these positions would be γ - and δ - to one of the carboxyl groups in strychninonic acid, and this acid does not appear to have any tendency to yield a lactone. So far no definite experimental evidence is available to enable us to select with any certainty either of the remaining positions *d* or *e*, but we have

chosen *c* as the result of a comparison of strychnine with quinine and other natural products in which a similar grouping occurs.

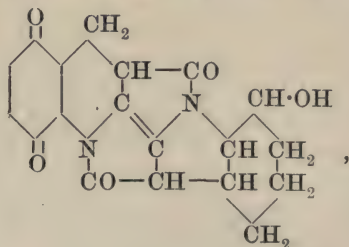
This argument, based on lactone formation, might appear to apply also to a hydroxyl group in the position *c*, but the examination of a model shows that a hydroxyl group in this position is too far removed from the carboxyl group to make lactone formation probable.

The formula which we have suggested for strychninonic acid leads to the following expressions for strychninolic acid and strychninolone:

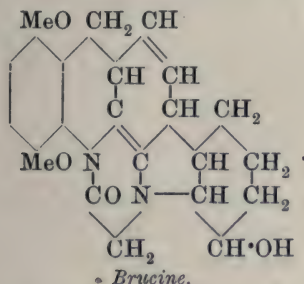


and these also appear to agree in a satisfactory manner with the properties of these substances so far as they have been investigated. A possible objection to the formula assigned to strychninolone is the stability of this substance towards oxidising agents, which may not be considered compatible with the presence of the $\text{:CH}\cdot\text{OH}$ group, but, in our opinion, this argument does not carry much weight.

It has already been pointed out (p. 309) that brucine is dimethoxystrychnine, and the positions of the methoxy-groups in the benzene nucleus seem to be fixed by the observation of Leuchs and Weber (*Ber.*, 1909, **42**, 3709) that brucinolone is readily oxidised by nitric acid, with elimination of the methoxy-groups and formation of a quinone which crystallises in red needles, and yields a quinol on reduction with sulphurous acid. Since an *o*-quinone would hardly be produced under these conditions, it is probable that the substance is a *p*-quinone of the constitution:



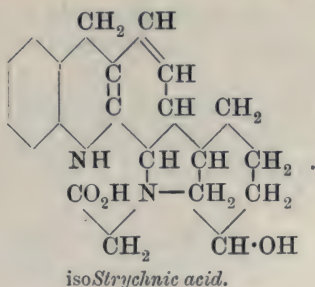
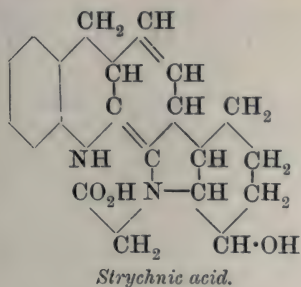
and its formation is a strong indication that the methoxy-groups occupy the position assigned to them in the following formula for brucine:



One other very interesting point in connexion with strychnine and brucine which we have already mentioned (p. 305) is the behaviour of these alkaloids on hydrolysis. When strychnine is digested with sodium methoxide or barium hydroxide, it yields strychnic and *isostrychnic* acids:

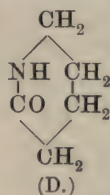
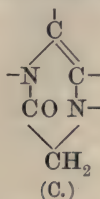


and these isomeric acids are converted by the action of heat into the isomeric alkaloids, strychnine and *isostrychnine*. Brucine exhibits an exactly similar behaviour. Strychnic and *isostrychnic* acids resemble each other so closely in all their reactions that it might at first sight appear that they were simply stereoisomeric modifications of the same substance. The conversion of these acids into the isomeric strychnines is, however, scarcely in accordance with this view, and it is far more probable that the isomerism is due to a difference in the position of one of the double linkings in the molecule, probably in the sense represented by the formulæ:



If the formulæ suggested for strychnine and brucine be examined with the view of discovering some reason for the extremely poisonous

nature of these alkaloids, it would seem that the only section to which this property can be ascribed is the grouping (C):

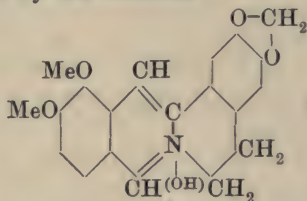


containing the two nitrogen atoms. Schotten (*Ber.*, 1888, **21**, 2244) has called attention to the fact that α -ketopiperidine (α -piperidone) (D) has poisonous properties of the same kind as those exhibited by strychnine and brucine, and it is not at all improbable that the introduction of the second nitrogen atom into this molecule may have the effect of much intensifying these poisonous properties.

We are at present engaged in synthesising substances containing the above di-nitrogen group, and propose to have these examined in order to find out whether they have poisonous properties similar to those of strychnine and brucine.

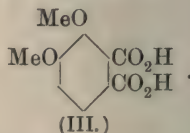
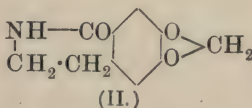
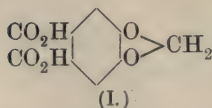
II.—*Berberine, Corydaline, and Allied Alkaloids.*

The constitution of berberine, $C_{20}H_{17}O_4N$, is generally accepted as being represented by the formula:



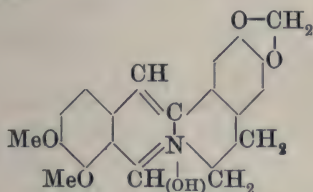
and this formula is based on the investigation of the long series of products which result from the degradation of the molecule by oxidation with permanganate (*Trans.*, 1889, **55**, 63; 1890, **57**, 992).

The position of the methylenedioxy-group* is determined by the fact that hydrastic acid (I) and ω -aminoethylpiperonylcarboxylic anhydride (II) are found among the products of this oxidation:



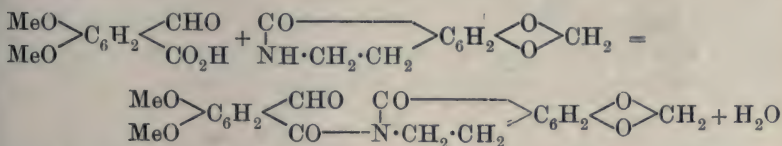
* It is unfortunate that this group should have been wrongly placed in the original papers.—W. H. P., jun.

On the other hand, the fact that hemipinic acid (III) is produced in considerable quantities during the oxidation of berberine does not definitely fix the positions of the methoxy-groups, since the formula for berberine:

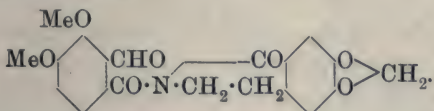


would also account for the formation of hemipinic acid on oxidation.

On carefully considering this matter, it appeared to us that the only oxidation product of berberine which is able to afford definite information as to the position of these methoxy-groups is *berberal* (Trans., 1890, 57, 1000 and 1062). This substance, on hydrolysis, yields ψ -opianic acid and ω -aminoethylpiperonylcarboxylic anhydride, and conversely it may be synthesised by simply heating ψ -opianic acid and ω -aminoethylpiperonylcarboxylic anhydride at 180° . When this experiment was described (*loc. cit.*, p. 1079), this important synthesis was assumed to take place according to the equation:



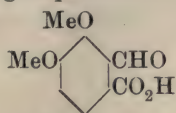
and it was suggested (p. 1002) that the constitution of *berberal* must be represented thus:



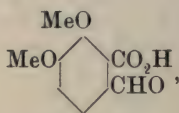
The formula for berberine itself, given at the commencement of this section, was largely based on this constitutional formula for *berberal*. ψ -Opianic acid was first obtained as the result of these experiments on the oxidation of berberine, and, as it is difficult to prepare in any quantity by this process, and no other method of preparation has yet been discovered, the mechanism of its condensation with basic substances has not been investigated in detail.

If, however, the formulæ of ψ -opianic acid is compared with that of opianic acid, it will be seen that they are both *o*-aldehydo-

acids, and differ only in the positions of these groups relative to the methoxy-groups:



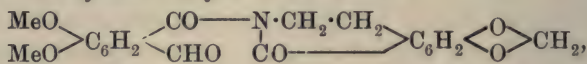
ψ -Opianic acid.



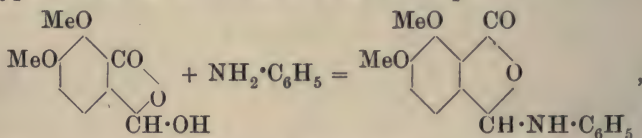
Opianic acid.

and as this is the only difference in constitution, it may be safely assumed that they will behave in an exactly similar manner when taking part in reactions characteristic of *o*-aldehyde-acids.

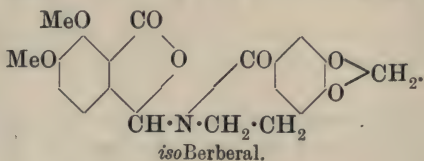
Important evidence in support of this view has already been obtained, since it was shown in the earlier papers (Trans., 1890, 57, 1081) that opianic acid condenses with ω -aminoethylpiperonyl-carboxylic anhydride to yield a substance:



which has properties exactly similar to those of berberal, and was therefore named *isoberberal*. During recent years opianic acid has been the subject of detailed investigation, and the results which have been obtained necessitate a modification of our views as to the constitution of *isoberberal*, and consequently of berberal and of berberine itself. Liebermann (*Ber.*, 1886, 19, 2284; 1896, 29, 175) has shown that opianic acid reacts with aniline in the cold to yield anilino-opianic acid, and expressed the opinion that, during this process, the opianic acid reacts as a derivative of hydroxyphthalide in accordance with the equation:

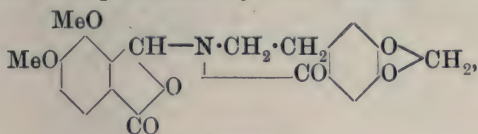


and from the study of this and many other similar condensations, it is clear that, in condensations of opianic acid with basic substances, it is always the carbon atom of the aldehyde group which is attached to the nitrogen atom in the final product. There can be little doubt that a similar process takes place when opianic acid reacts with ω -aminoethylpiperonylcarboxylic anhydride to yield *isoberberal*, and the constitution of this substance is therefore not that originally assigned to it (p. 319), but must be modified to:



Furthermore, since ψ -opianic acid is so exactly similarly constituted to opianic acid, and exhibits in all its reactions so close an analogy with this acid, it cannot be doubted that, when it condenses with basic substances, it also reacts in a similar manner.

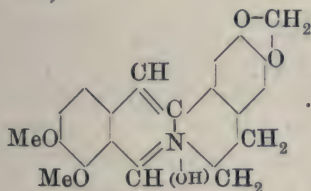
It follows, therefore, that in the formation of berberal by the condensation of ψ -opianic acid with ω -aminoethylpiperonylcarboxylic anhydride, the aldehydic carbon atom of the ψ -opianic acid becomes combined with the nitrogen atom, and the constitution of berberal must therefore be represented by the formula:



Berberal.

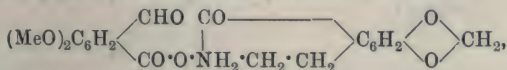
and not by that originally assigned to it (p. 319).*

This new expression is in complete agreement with the properties of berberal, and its acceptance involves the alteration of the position of the methoxy-groups in the old berberine formula (p. 318), so that the constitution of the alkaloid must now be written (compare p. 319):

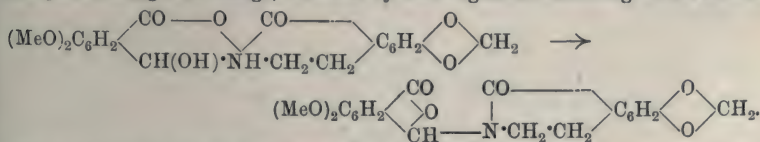


Berberine.

* The actual mechanism of the condensation of opianic acid or ψ -opianic acid with basic substances is probably not so simple as that suggested by Liebermann (*loc. cit.*). When the syntheses of berberal and *isoberberal* were described (Trans., 1890, 57, 1080 and 1082), it was proved that in both cases the first step is the formation of the salt of the acid with the base. Thus, for example, ψ -opianic acid combines with ω -aminoethylpiperonylcarboxylic anhydride to form the salt,

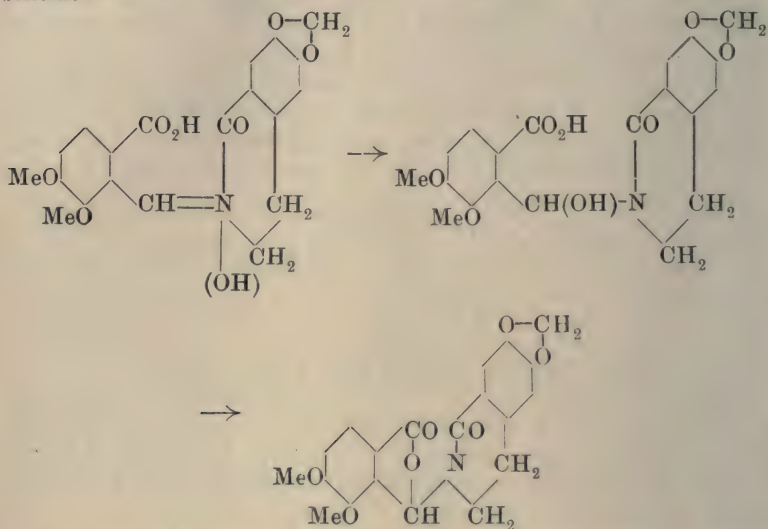


which, when heated at 180°, yields berberal. Most probably aldol formation first takes place during this change, followed by rearrangement according to the scheme :

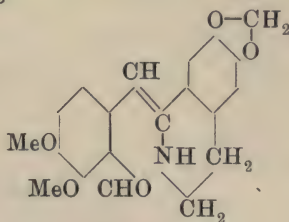


The synthesis of *isoberberal* takes place in an exactly similar manner, and it is very probable that all such condensations between opianic acid or ψ -opianic acid and basic substances proceed on similar lines.

The formation of berberal by the oxidation of berberine is now easy to understand, and evidently takes place according to the scheme:



The salts of berberine are derived from the hydroxyl formula given above (compare J. Gadamer, *Arch. Pharm.*, 1905, **243**, 31), but there is reason to believe that the alkaloid itself exists in the corresponding aldehyde modification. Gadamer (*Chem. Zeit.*, 1902, **26**, 291) has shown that, when berberine sulphate is treated with barium hydroxide, it yields a brownish-red, strongly alkaline solution, which doubtless contains the hydroxy-modification of berberine. If, however, this solution is mixed with excess of sodium hydroxide, a yellow modification of berberine is obtained, which apparently has the properties of an aldehyde, and Gadamer has named this modification *berberinal*. The constitution of this modification, based on the new formula for berberine which we have proposed, will be the following:

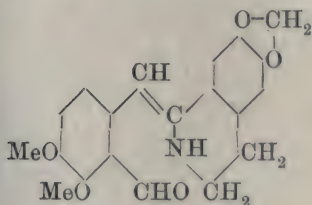


Berberinal.

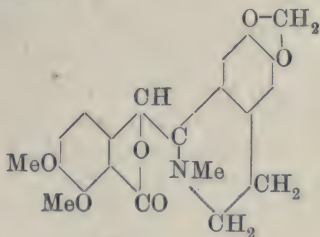
Berberinal yields an oxime, reacts with magnesium alkyl iodides with formation of homologues of berberine (Freund and Beck, *Ber.*,

1904, 37, 3336 and 4673), and, when treated with a large excess of alkali, is reduced to dihydroberberine and simultaneously oxidised to hydroxyberberine, the aldehyde grouping being converted into $\cdot\text{CH}_2(\text{OH})$ and $\cdot\text{CO}_2\text{H}$ in the manner characteristic of aromatic aldehydes.

The proposed modification of the positions of the methoxy-groups in the berberine formula receives further confirmation from the consideration that berberine occurs along with hydrastine in *hydrastis canadensis*, and the close relationship between these alkaloids becomes very striking if the new formula for berberinal is placed by the side of that of hydrastine:



Berberinal.



Hydrastine.

These alkaloids are, indeed, so closely related as to suggest that hydrastine is either formed in the plant from berberine, or that they are both derived from some common parent.

THE UNIVERSITY,
MANCHESTER.

XXXIV.—*Decomposition of Dimercurammonium Nitrite by Heat.*

By PRAFULLA CHANDRA RAY and ATUL CHANDRA GHOSH.

THE preparation of dimercurammonium nitrite has been already described at some length (*Trans.*, 1902, 81, 644), and evidence has been adduced in support of the view that it is a derivative of ammonium nitrite.

The solution of sodium mercuric nitrite, from which it is obtained by the action of ammonia, does not contain mercury as cation, but as part of a complex anion; it does not, therefore, undergo the hydrolysis so characteristic of oxylic mercuric salts, and has presumably a non-oxylic constitution. Two samples of the salt were prepared, and dried at 95° for analysis:

Found : Hg = (I) 84.74 ; (II) 84.61. N = (I) 6.33 ; (II) 6.16.

$\text{NH}_2\text{NO}_2, \frac{1}{2}\text{H}_2\text{O}$ requires Hg = 85.29. N = 5.97 per cent.

Method of Experiment.—From 0.2 to 0.6 gram of salt was placed in a small bulb, the drawn-out stem of which was connected with a Sprengel pump. A preliminary trial proved that the salt commenced to decompose, although very slowly, at about 140° , and that even at 210° a portion of it remained undecomposed. The bulb was therefore cautiously and gradually immersed in a bath of molten sodium and potassium nitrates, mixed in about equal proportions (m. p. 218°). The temperature was slowly raised to 250° , when no more gas was evolved, the “click” in the fall-tube remaining persistent. Raising the temperature to 280° made no difference in this respect. The gas which was evolved was found to consist of a mixture of nitrous oxide, nitrogen, and oxygen; nitrous fumes were not noticed; in fact, the mercury in the fall-tube was not in the least tarnished, nor could even a trace of nitric oxide be detected. If, however, the bulb was suddenly plunged in a bath previously heated to 225° , the mode of decomposition was slightly different. Mercury in the shape of fine dust was at once deposited on the glass, and in the gaseous mixture nitric oxide could be recognised.

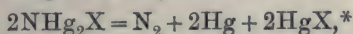
The nitrous oxide was removed by alcohol, and sometimes by repeated shaking with cold water, until no more absorption took place. The oxygen was in some instances removed by alkaline pyrogallate, but generally by means of phosphorus. The residue in the bulb was of a greyish-yellow colour; it consisted mainly of mercuric oxide with a small proportion of mercuric nitrate. This was proved by boiling the mixture with a solution of sodium hydroxide. The filtrate indicated the presence of nitrogen in the form of nitrate. Metallic mercury, both as a mirror and in fine globules, was deposited in the stem of the bulb. More than a dozen experiments were performed, the results of some of which are tabulated below :

“Free” N.	N as N_2O .	N as $\text{Hg}(\text{NO}_3)_2$.	Oxygen.	Total O in the salt.	Hg as $\text{Hg}(\text{NO}_3)_2$.	Hg as HgO .	“Free” Hg.
I. 3.21	1.55	1.21	0.21	6.82	8.64	57.20	19.45
II. 3.17	1.48	1.32	0.17	—	9.43	55.31	20.55
III. 3.43	1.44	1.10	0.22	—	—	—	—
IV. 3.53	1.60	0.84	0.34	—	6.00	62.65	16.68
V. 3.73	1.52	0.72	0.25	—	5.14	63.31	16.84

In those experiments in which nitric oxide was obtained, the nitrogen was distributed as follows :

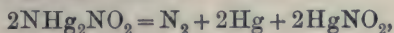
	“Free” N.	N as N_2O .	N as $\text{Hg}(\text{NO}_3)_2$.	N as NO.
I.	2.54	1.03	2.31	0.09
II.	3.22	2.24	0.29	0.22
III.	2.69	1.95	0.95	0.38

Discussion of Results.—It has already been pointed out that the halogen derivatives of the mercurammonium group (NHg_2^-) may be regarded as non-oxylie in constitution, since they decompose under the action of heat according to the equation :

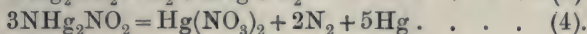
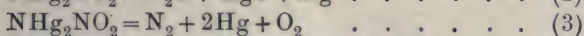
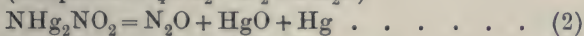
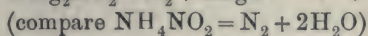


where $\text{X} = \text{Cl}$ or Br .

From analogy, one would naturally expect that the nitrite of the series should decompose as follows :



and that the mercurous nitrite thus formed, being unstable at this temperature, would yield its own products of decomposition (compare Rây and Sen, *Trans.*, 1903, **83**, 491). We have repeated the experiment on the decomposition of mercurous nitrite. The initial temperature of decomposition has been found to be almost the same as that of dimercurammonium nitrite, namely, 140° , and it is completed at 247° . In order to protect the mercury in the Sprengel pump from being soiled, a glass spiral, packed with glass beads and moistened with sodium hydroxide solution, was interposed, as in some of the previous experiments (compare *Trans.*, 1905, **87**, 180). The gaseous product which was collected was found to be nitric oxide. Moreover, had dimercurammonium nitrite decomposed according to the equation given above, exactly half the nitrogen would have been given off as "free" nitrogen, but it varies from 3.2 to 3.7 per cent. The formation of nitrous oxide is rather remarkable. The reaction evidently seems to proceed in three or four directions simultaneously, which may be expressed by the following equations :



We are at present engaged in studying the decomposition of dimercurammonium nitrate, in the hope that further light may be thrown on these points.

CHEMICAL LABORATORY,
PRESIDENCY COLLEGE, CALCUTTA.

* Rây, "Studien über die Konstitution der Dimerkurammonium Salze" (*Zeitsch. anorg. Chem.*, 1902, **33**, 193; also, Sen, *ibid.*, 197).

XXXV.—*The Double Nitrites of Mercury and the Metals of the Alkaline Earths.*

By PRAFULLA CHANDRA RÂY.

IN a previous communication a general method of preparation of the double nitrites of mercury and the alkali metals has been described (Trans., 1907, 91, 2031). Recently it has been found that this method is equally applicable to the preparation of the corresponding mercuric calcium, mercuric strontium, and mercuric barium nitrites. For instance, if a solution of calcium nitrite is added to a perfectly clear solution of mercurioso-mercuric nitrite, $(\text{HgNO}_2)_2, 4\text{Hg}(\text{NO}_2)_2$, almost immediate turbidity is caused, due to the separation of metallic mercury in a fine state of division. The explanation already given (*loc. cit.*), namely, that "the process of dissociation is accelerated because of the tendency of one of the products of dissociation, namely, mercuric nitrite, to unite with the alkali nitrite," admits of further amplification. It is the tendency to form complex ions that is really the *motif* of the reaction. A solution of potassium mercuric nitrite, $\text{K}_2\text{Hg}(\text{NO}_2)_4$, contains mercury, not as a cation, but as part of a complex bivalent anion, $\text{Hg}(\text{NO}_2)_4$.* Hence, such a solution behaves as a neutral one, and can be diluted *ad infinitum* without undergoing the hydrolysis, so characteristic of the oxy-salts of mercury, for example, mercuric nitrate. This also explains the singular behaviour which I noticed some twelve years ago (*Zeitsch. anorg. Chem.*, 1896, 12, 367), namely, that carbamide does not precipitate the mercury from the solution, or a solution of sodium sulphate give the characteristic precipitate of turpeth mineral.

Method of Preparation.—The light yellow solution of the double nitrites is evaporated under diminished pressure over sulphuric acid. As a rule, crystallisation of the salts does not take place, but a syrupy liquid is obtained, which, on being stirred with a rod, solidifies entirely, with the formation of mealy crystals and liberation of heat. In fact, the characteristic behaviour of supersaturated solutions is noticed. As the crystals were very soluble, they were washed with the minimum quantity of water, and dried by pressure between folds of bibulous paper. If the salts are preserved in a stoppered bottle without being well dried, they slowly decompose, with evolution of nitrous fumes; but if they are kept in the open bottle in the desiccator, they remain perfectly stable (compare mercuric

* Hans Pick, "Beiträge zur Charakteristik des Nitrit-ions. Der Quecksilber nitrit-komplex" (*Diss.*, Breslau, 1906).

nitrite, Trans., 1904, 85, 524). The compounds described below contain five molecules of water of crystallisation.

Mercuric Calcium Nitrite.

Found: $\text{Hg} = 38.21$; $\text{Ca} = 7.96$; $\text{N} = 10.98$.

$\text{Hg}(\text{NO}_2)_2, \text{Ca}(\text{NO}_2)_2, 5\text{H}_2\text{O}$ requires $\text{Hg} = 38.91$; $\text{Ca} = 7.78$;
 $\text{N} = 10.90$ per cent.

Mercuric Strontium Nitrite.

Found: $\text{Hg} = 44.58$; $\text{Sr} = 13.08$; $\text{N} = 11.17$.

$3 \text{Hg}(\text{NO}_2)_2, 2\text{Sr}(\text{NO}_2)_2, 5\text{H}_2\text{O}$ requires $\text{Hg} = 45.31$; $\text{Sr} = 13.18$;
 $\text{N} = 10.57$ per cent.

Mercuric Barium Nitrite.

Found: $\text{Hg} = 39.88$; $\text{Ba} = 19.80$; $\text{N} = 10.55$.

$3\text{Hg}(\text{NO}_2)_2, 2\text{Ba}(\text{NO}_2)_2, 5\text{H}_2\text{O}$ requires $\text{Hg} = 42.13$; $\text{Ba} = 19.24$;
 $\text{N} = 9.84$ per cent.

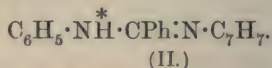
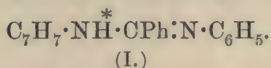
The preparation of the last two salts was repeated, but the composition was practically constant. The low percentage of mercury and the proportionately high percentages of barium and of nitrogen in the last one are probably due to the substance being invariably contaminated with traces of mother liquor containing excess of the nitrites of the latter metal.

On comparing the whole series of double nitrites, it is of interest to note that the power of mercuric nitrite to unite with the nitrites of the alkali metals is the greater the less the atomic weights of the latter. Thus, mercuric nitrite can combine with four molecules of lithium nitrite and with three molecules of potassium nitrite, although it also forms characteristic stable compounds with two molecules of either sodium or potassium nitrite. On the other hand, it combines molecule for molecule with calcium nitrite. Again, one molecule of mercuric nitrite can combine with only two-thirds of a molecule of strontium or barium nitrite. Cryoscopic determinations of the molecular weights of the above salts have been undertaken with the view of throwing light on their constitution, the results of which I hope to communicate shortly.

XXXVI.—*The Constitution of the Amidines. A New Method for Determining Molecular Symmetry.*

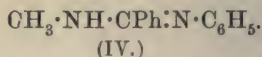
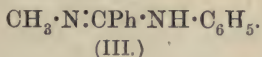
By JULIUS BEREND COHEN and JOSEPH MARSHALL.

H. VON PECHMANN (*Ber.*, 1895, 28, 869) made the observation that the amidine (I) prepared from benzanilide iminochloride and *p*-toluidine was identical, so far as could be shown by comparison of melting points and other physical properties with the amidine (II) obtained from benzoyl-*p*-toluidide iminochloride and aniline.



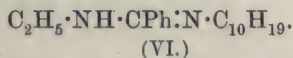
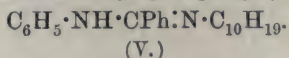
The product obtained by the ethylation of this substance was shown to be a mixture of two ethyl derivatives in equal quantities, and these were separable by mechanical means. This fact may indicate, either that the original amidine is a mixture of equal quantities of the substances represented by (I) and (II), or that it has a varying structure caused by the oscillation of the hydrogen atom marked * in the formula between the two nitrogen atoms.

In cases where the two bases differed in character from each other, von Pechmann obtained quite different results. Using (*a*) methylbenzamide iminochloride and aniline, and (*b*) benzanilide iminochloride and methylamine, he obtained, as before, the same product in each case, but methylation of this substance produced only one methyl derivative. This was found to be identical with the amidine obtained by combining methylbenzamide iminochloride with methylaniline, indicating that the amidine prepared either by method (*a*) or (*b*) had the constitution represented by (III), and that a substance with the formula (IV) was not produced at all.



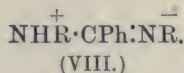
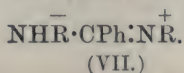
The present investigation was undertaken with the view of determining whether the introduction of optically active groups into the amidine would afford a more delicate means of distinguishing between the products of the two reactions in the event of their being indistinguishable by other means. The optically active base used in most of the experiments was *l*-menthylamine, as being easily obtainable in large quantities (Tutin and Kipping, *Trans.*, 1904, 85, 69). The benzoyl derivative of menthylamine was converted into the iminochloride and allowed to react with the second base, and the amidine obtained in this way was compared with that prepared from the iminochloride of the benzoyl derivative of the second base and menthylamine. The

other bases used were aniline, *o*-, *m*-, and *p*-toluidine, and ethylamine. It was found that in all cases the pairs of amidines had exactly the same specific rotations, melting points, and other physical properties. It was also shown, by ethylation of some of the amidines, that they were single substances and not mixtures, as only one ethyl derivative was formed in each case. These ethyl derivatives were also synthesised, and it was proved that the constitution of the amidine containing phenyl and menthyl groups is represented by (V), and that containing ethyl and menthyl groups by (VI).

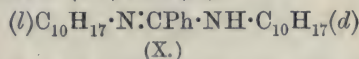
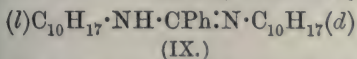


These experiments confirm the observation that marked difference in character of the radicles causes the formation of one and the same product in the two reactions, and there is no indication of any equilibrium mixture, as in the case where the radicles are of the same type. It is interesting to note that the hydrogen atom is in all cases attached to the nitrogen atom in the less basic group.

It was then thought that it would be of interest to prepare an amidine in which the two bases were enantiomorphous. In such a case, according to von Pechmann, a mixture of two substances would be obtained of the types (VII) and (VIII).



These should be produced in equal quantities, and hence any optical activity due to (VII) would be counterbalanced by that due to (VIII), and the product should be inactive. This was found to be the case, the bases used being *d*- and *l*-bornylamines, which are easily obtained by Forster's method (Trans., 1898, 73, 390) from the corresponding camphors. Ethylation of the amidine produced one inactive ethyl derivative. It was conceivable that if the amidine were a mixture of two substances represented by formulæ (IX) and (X) :



it might be possible by crystallising it with an optically active acid to obtain fractions which would, after removal of the acid, be active. The amidine was combined with Reychler's *d*-camphorsulphonic acid, and the salt crystallised several times from hot light petroleum. The specific rotations of various fractions were then determined, but they were found to be practically identical. After removal of the acid, the recovered amidine was inactive. Similar experiments were carried out with the ethyl derivative, but no resolution of the amidine could be detected.

It is proposed to extend to other classes of compounds this method

of examining molecular symmetry by introducing enantiomorphous radicles into different positions in the molecule. We are at present engaged in determining the space formula of quinquivalent nitrogen by the aid of this method.

EXPERIMENTAL.

Phenylmenthylbenzamidine, $C_{10}H_{19} \cdot N : C(C_6H_5) \cdot NH \cdot C_6H_5$, was prepared by boiling in light petroleum the iminochloride obtained from 5 grams of benzanilide with 7.5 grams of *l*-menthylamine. The menthylamine hydrochloride which separated was collected, the light petroleum removed, and the gummy residue extracted with dilute hydrochloric acid. To the filtered acid solution, sodium hydroxide was added, and the amidine extracted with ether. It was crystallised from alcohol, and formed fine needles melting at $110-111^\circ$:

0.5072 in 20 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 7.40^\circ$;
whence $[\alpha]_D^{15} - 146^\circ$.

The same compound was obtained by boiling the light petroleum solution of the iminochloride from 5 grams of benzoylmenthylamide with 3.6 grams of aniline. The hydrochloride of the amidine which separated was collected, washed with a little more ether, and decomposed with sodium hydroxide. The compound obtained after recrystallisation from alcohol melted at $110-111^\circ$, and a mixture of this substance with that obtained in the previous experiment had the same melting point:

0.5104 in 20 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 7.44^\circ$;
whence $[\alpha]_D^{15} - 146^\circ$.

0.2054 gave 15 c.c. N_2 at 15° and 750 mm. $N = 8.61$.

$C_{23}H_{30}N_2$ requires $N = 8.39$ per cent.

The *hydrochloride*, prepared from both specimens, melted at 224° , and formed long needles when crystallised from dilute alcohol. It was only slightly soluble in cold, but fairly so in hot, water.

The *platinichloride* was precipitated in a crystalline condition by adding platinic chloride to a dilute alcoholic solution of the hydrochloride. It melts at 213° :

0.5504 gave 0.0998 Pt. M.W. of amidine = 333.

$C_{23}H_{30}N_2$ requires M.W. = 334.

Ethylation of Phenylmenthylbenzamidine.

2.3 Grams of the pure amidine were heated on the water-bath for ten hours with an excess of ethyl iodide, the latter being then distilled. The residue, consisting of the hydriodide of the ethylated amidine, crystallised, and was decomposed with sodium hydroxide. After two

crystallisations from alcohol, 1.9 grams of pure substance were obtained in beautiful square plates, which melted at 66—67°. The substance was perfectly homogeneous :

0.3596 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 11.28^\circ$;
whence $[\alpha]_D^{25} - 392^\circ$.

0.6260 in 25 c.c. chloroform gave, in a 0.302-dcm. tube, $\alpha_D - 2.95^\circ$;
whence $[\alpha]_D^{25} - 391^\circ$.

This amidine was also produced by treating benzoylmenthylamide iminochloride with ethylaniline. The characteristic plates, melting at 66—67°, were obtained :

0.4611 in 25 c.c. chloroform gave, in a 2-dcm. tube, $[\alpha]_D - 14.47^\circ$;
whence $[\alpha]_D^{25} - 392^\circ$.

0.2164 gave 14.55 c.c. N_2 at 15° and 749 mm. $N = 7.92$.

$C_{25}H_{34}N_2$ requires $N = 7.73$ per cent.

The *hydrochloride* was not obtained in the crystalline condition, but only as a sticky mass, soluble in water. The *hydriodide* crystallises in prisms, melting at 220° . The *platinichloride* was precipitated from an aqueous solution of the hydrochloride, and melted at 151° :

0.5756 gave 0.0980 Pt. M.W. of amidine = 368.

$C_{25}H_{34}N_2$ requires M.W. = 362.

Phenylmenthylethylbenzamidine.

For purposes of comparison, the amidine from benzanilide iminochloride and ethylmenthylamine was prepared. It crystallised from alcohol, in which it was much less soluble than the preceding substance, in needles melting at 157° :

0.7436 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 3.6^\circ$;
whence $[\alpha]_D^{25} - 60.5^\circ$.

0.1645 gave 11 c.c. N_2 at 20° and 762 mm. $N = 7.73$.

$C_{25}H_{34}N_2$ requires $N = 7.73$ per cent.

The *hydrochloride* was insoluble in cold water, and crystallised from alcohol in needles melting at 280° .

o-Tolylmenthylbenzamidine, $C_{10}H_{19} \cdot N : C(C_6H_5) \cdot NH \cdot C_7H_7$.

This substance, prepared from benzoyl-*o*-toluidide iminochloride and menthylamine, was isolated as the hydrochloride by saturating with dry hydrogen chloride the light petroleum solution from which the precipitated menthylamine hydrochloride formed in the reaction had been separated. The precipitated gummy mass was crystallised from alcohol and decomposed with dilute aqueous sodium hydroxide. The amidine crystallises from alcohol in needles melting at 106—107° :

0.3391 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 2.85^\circ$;
whence $[\alpha]_D^{14^\circ} - 105^\circ$.

This amidine was also prepared from benzoylmenthylamide iminochloride and *o*-toluidine, the hydrochloride of the amidine separating from the light petroleum almost quantitatively:

0.6264 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.26^\circ$;
whence $[\alpha]_D^{14^\circ} - 105^\circ$.

0.2044 gave 13.9 c.c. N_2 at 11° and 750 mm. $N = 8.13$.

$C_{24}H_{32}N_2$ requires $N = 8.05$ per cent.

The *hydrochloride* crystallises from alcohol in small, rectangular plates, melting at 218° , and is scarcely soluble in water.

The *platinichloride* was obtained as a crystalline powder:

0.5654 gave 0.1005 Pt. M.W. of amidine = 344.

$C_{24}H_{32}N_2$ requires M.W. = 348.

m-Tolylmenthylbenzamidine was isolated in a similar manner to the *o*-tolyl derivative from benzoylmenthylamide iminochloride and *m*-toluidine. The base crystallises from alcohol in needles, and melts at $89-90^\circ$:

0.6268 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 7.13^\circ$;
whence $[\alpha]_D^{14^\circ} - 142^\circ$.

The amidine from benzoyl-*m*-toluidide and menthylamine had the same melting point:

0.6118 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.98^\circ$;
whence $[\alpha]_D^{14^\circ} - 143^\circ$.

0.2090 gave 14.4 c.c. N_2 at 13.5° and 751 mm. $N = 8.18$.

$C_{24}H_{32}N_2$ requires $N = 8.05$ per cent.

The *hydrochloride* crystallises from alcohol, and is only very slightly soluble in hot water. It melts at 232° .

The *platinichloride* forms very small needles, which melt at 217° :

0.5603 gave 0.0991 Pt. M.W. of amidine = 346.

$C_{24}H_{32}N_2$ requires M.W. = 348.

p-Tolylmenthylbenzamidine, isolated in the usual way from benzoylmenthylamide iminochloride and *p*-toluidine, crystallised from alcohol in stout prisms, which melted at $63-68^\circ$ even after several recrystallisations:

0.6252 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.55^\circ$;
whence $[\alpha]_D^{14^\circ} - 131^\circ$.

Repeated crystallisation had no effect on this value. When prepared from benzoyl-*p*-toluidide and menthylamine, the same rather indefinite melting point was observed:

0.6231 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.54^\circ$;
whence $[\alpha]_D^{14^\circ} - 131^\circ$.

0.2069 gave 13.9 c.c. N_2 at 15° and 747 mm. $N = 7.94$.

$C_{24}H_{32}N_2$ requires $N = 8.05$ per cent.

The *hydrochloride* crystallised from alcohol in small needles melting at 225° , and the *platinichloride*, obtained as a crystalline precipitate, melted at 208° :

0.2700 gave 0.0474 Pt. M.W. of amidine = 350.

$C_{24}H_{32}N_2$ requires M.W. = 348.

Menthylethylbenzamidine, $C_{10}H_{19} \cdot N : C(C_6H_5) \cdot NH \cdot C_2H_5$.

This substance was prepared by treating a light petroleum solution of ethylamine (2 mols.) with the calculated quantity of benzoylmenthylamide iminochloride. The ethylamine hydrochloride was collected, and, after removal of the light petroleum, the gummy residue was boiled with dilute sulphuric acid. The clear solution of the sulphate was treated with a concentrated aqueous solution of potassium iodide, and the precipitated iodide was separated and decomposed with sodium hydroxide. The amidine solidified after removal of the ether used in its extraction, but all attempts at recrystallisation were unsuccessful. The substance melted at $65-67^\circ$. It was purified by conversion into the iodide, which was again decomposed. No alteration in the melting point could be observed:

0.6282 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.63^\circ$;
whence $[\alpha]_D^{12^\circ} - 112^\circ$.

The amidine was also prepared from ethyl benzamide iminochloride and menthylamine, and this specimen had the same melting point:

0.6240 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 5.57^\circ$;
whence $[\alpha]_D^{12^\circ} - 112^\circ$.

0.2133 gave 16.9 c.c. N_2 at 13° and 750 mm. $N = 9.49$.

$C_{19}H_{30}N_2$ requires $N = 9.80$ per cent.

The *hydrochloride* was only obtained as a sticky mass, which was very soluble in water. The *hydriodide*, which was much less soluble, was not obtained in a crystalline condition.

The *platinichloride* formed microscopic plates, melting at 218° :

0.4816 gave 0.0968 Pt. M.W. of amidine = 280.

$C_{19}H_{30}N_2$ requires M.W. = 286.

Four grams of this amidine were boiled for ten hours with ethyl iodide, and, after distilling off the excess of alkyl iodide, the *hydriodide* of *menthildiethylbenzamidine* which remained was recrystallised from water and then converted into the amidine. On crystallisation from alcohol, this formed small, rectangular plates, melting at $31-32^\circ$:

0.4756 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.53^\circ$;
whence $[\alpha]_D^{14^\circ} - 172^\circ$.

This substance was quite homogeneous, and proved to be identical with the amidine prepared from benzoylmenthylamide and diethylamine:

0.4709 in 25 c.c. chloroform gave, in a 2-dcm. tube, $\alpha_D - 6.47^\circ$; whence $[\alpha]_D^{14} - 172^\circ$.

The *hydrochloride* was not crystalline, but the *hydriodide* crystallised from water in fine needles, which melted at 155° . The *platinichloride* melts at 180° .

Before the enantiomorphous bornylamines were selected for use in the final experiments, several attempts were made to prepare other enantiomorphous bases.

d-Dihydrocarvylamine was prepared from *d*-carvone by reduction of the oxime with sodium in alcoholic solution (Wallach, *Ber.*, 1891, 24, 3984), and the *lævo*-base was obtained from *d*-limonene by way of the nitrosochloride and *l*-carvoneoxime. The benzoyl derivatives were prepared, but it was found that during the reaction of phosphorus pentachloride with these substances, hydrochloric acid is added on to the molecule, and hence the use of an unsaturated base was out of the question.

As the enantiomorphous carvones are easily obtained, it was thought that the carvomenthylamines prepared by the same methods from each of these carvones would answer our purpose. Accordingly, some time was spent in attempts to obtain these bases in quantity. Baeyer's method (*Ber.*, 1893, 26, 822) was first tried, but as very unsatisfactory yields were always obtained, the method was abandoned.

Attempts were made to reduce dihydrocarvylamine to tetrahydrocarvylamine by Sabatier and Senderens' method, but, although reduction took place to some extent, the reduced product was inactive. Next, 2-amino-1-methylcyclohexane was prepared from 1-methylcyclohexan-2-one, obtained from *o*-cresol (Sabatier and Mailhe, *Compt. rend.*, 1905, 140, 350), and an attempt was made to resolve this base by fractional crystallisation of the *d*-camphorsulphonate. No satisfactory results were obtained.

Finally, the two bornylamines were prepared. The active benzoyl derivative melts at 139° , and the inactive substance at 144° .

d-Bornyl-1-bornylbenzamidine.

The iminochloride of benzoyl-*l*-bornylamide was prepared in the usual way, and treated with a light petroleum solution of *d*-bornylamine. The amidine was isolated and crystallised from alcohol, from which it separated in small prisms (often in stellate clusters), melting at $93-94^\circ$.

The substance was optically inactive. It agreed in every respect with the amidine from benzoyl-*d*-bornylamide iminochloride and *l*-bornylamine :

0.2013 gave 12.4 c.c. N_2 at 12.5° and 731 mm. $N = 7.15$.

$C_{27}H_{40}N_2$ requires $N = 7.14$ per cent.

The *hydrochloride* crystallises from ether in long needles, which melt at 297° . It is very soluble in alcohol. The *platinichloride* melts at 215° . The *sulphate* was obtained as fine needles from dilute alcohol, and melted at 138° . The *hydriodide* is insoluble in water, crystallises easily from absolute alcohol, and melts at 262° .

The *d*-camphorsulphonate was prepared by mixing molecular proportions of the amidine and acid dissolved in ether and alcohol respectively. The salt was crystallised several times from light petroleum, and melted at $205\text{--}206^\circ$:

1.0353 in 25 c.c. alcohol gave, in a 2-dcm. tube, $\alpha_D + 1.34^\circ$; whence

$$[\alpha]_D^{16^\circ} + 16.2^\circ.$$

The salt was further recrystallised, but the melting point was not affected, and a determination of the specific rotation gave 16.4° . A second crop of crystals had a slightly lower melting point, and a specific rotation of 15.4° .

A quantity of the salt was mixed with ice-water, cold ether and cold sodium hydroxide solution added, and the ethereal solution of the amidine was immediately polarimetrically examined. No rotation could be observed.

Ethylation of d-Bornyl-l-bornylbenzamidine.

The amidine was heated in a sealed tube with light petroleum and excess of ethyl iodide for eight hours in a boiling-water bath. On cooling, the *hydriodide* of the ethylamidine crystallises in fine needles, melting at $257\text{--}258^\circ$, and these were recrystallised from a mixture of benzene and light petroleum and decomposed by sodium hydroxide. The amidine melted at $93\text{--}94^\circ$, and a mixture of this with the original amidine had a melting point of $91\text{--}93^\circ$. It was inactive :

0.1997 gave 12.4 c.c. N_2 at 14° and 711 mm. $N = 6.96$.

$C_{29}H_{44}N_2$ requires $N = 6.67$ per cent.

The *hydrochloride* crystallises from alcohol in needles, melting at 298° .

The *d*-camphorsulphonate was prepared as before and recrystallised ; it melts at $204\text{--}206^\circ$:

0.9987 in 25 c.c. alcohol gave, in a 2-dcm. tube, $\alpha_D + 1.27^\circ$; whence

$$[\alpha]_D^{16^\circ} + 16.1^\circ$$

The amidine recovered from this fraction of the salt was inactive,

as was also that obtained from the other fractions which were separately examined.

The authors have to thank Mr. W. H. Perkins for help in the preparation of the first amidine described in this paper.

THE UNIVERSITY,
LEEDS.

XXXVII.—*Silver Amalgams.*

By HENRY CHAPMAN JONES.

SILVER amalgams are of interest, not only because they are members of the general class of amalgams, but also because some occur in Nature, and because of the specific gravity of some of them being much higher than that of mercury. The remarkable contraction that takes place when the two metals combine was stated by Joule (*Journ. Chem. Soc.*, 1863, **16**, 383) to be "referable no doubt to the assumption of the solid state by the mercury, the specific gravity of which comes out at 16.5 from these (Joule's) experiments." This high value for the specific gravity of solid mercury does not appear to have been confirmed.

The silver amalgams that have so far been examined have been of very irregular compositions when viewed as compounds, and as they have been prepared by bringing the two metals together either directly, or by allowing an excess of mercury to precipitate silver on itself from a salt solution, it is hardly possible that the amalgams obtained were homogeneous.

The object of this paper is to indicate a method by which a series of silver amalgams may be obtained of definite molecular composition (within the errors of experiment) and in a really homogeneous condition; and, further, to give some of the properties of two of them.

The method consists, in short, in the preparation of a double salt, or a molecular mixture of salts, of the two metals with subsequent reduction in the cold to the metallic condition. When mercuric chloride acts on either silver or mercury, or an amalgam of the two metals, each atom of either metal combines with a molecule of mercuric chloride. If, then, the chlorine is removed, and this is easily done by means of ferrous oxalate, the metals alone remain. In this way amalgams may be obtained in which the metals exist in the proportions indicated by the formulæ AgHg , AgHg_3 , AgHg_7 , AgHg_{15} , AgHg_{31} , AgHg_{63} , and the author has actually prepared these six amalgams, although not all of them in

quantities suitable for examination. If the product of the action of mercuric chloride on metallic silver, that is, the double chloride, AgHgCl_2 , is treated with an excess of sodium sulphite solution, half the silver and three-fourths of the mercury will be dissolved, and there will remain an amalgam of the composition represented by the formula Ag_2Hg . This, by treatment alternately with mercuric chloride and ferrous oxalate, gives another series of amalgams intermediate between the members of the series given above, namely, Ag_2Hg , AgHg_2 , AgHg_5 , AgHg_{11} , etc.

Preparation of the Amalgams.

Some details concerning this have already been published (*J. Soc. Chem. Ind.*, 1893, **12**, 983). A granular sample of metallic silver reacts most readily with mercuric chloride—such preparations as are obtained by the reduction of silver salts by means of zinc in acid solutions, or by dextrose in the presence of alkali hydroxide. But metallic silver so obtained I have never found to be pure. If dried at 100° , it invariably loses something on ignition, 0.12, 0.74 per cent., and so on in different cases, although the product was well washed with dilute nitric acid and ammonia. Silver obtained by reduction with ammonium sulphite, if properly washed and dried at 100° , loses nothing on ignition, but such silver is flaky and crystalline rather than granular, and reacts less readily than the other. It is preferable, in using ammonium sulphite, to heat the mixture quickly in small portions, and so obtain the metal more finely divided than by the usual slow process.

Metallic silver and mercuric chloride will interact in many different liquids, or in no liquid, by simply shaking them together and allowing them to remain. I have always used water, but, judging from the analogous reaction with mercuric bromide, it might be possible to find a medium that would expedite the change. Mercuric bromide reacts very slowly in water, the salt being very sparingly soluble; but in benzene, in which the salt is soluble to practically the same extent, the velocity of the reaction is very remarkably increased, whilst in acetone, which very freely dissolves the mercuric bromide, the change does not appear to be so rapid as in benzene. Light petroleum dissolves much less of the mercuric salt than water does, yet under otherwise the same conditions the change will appear complete in light petroleum in a time that in water has sufficed for little more than a superficial reaction.

The reduction of the chloride by means of ferrous oxalate takes place practically at once. The reagent is obtained by pouring one volume of a saturated solution of ferrous sulphate into six volumes of a saturated solution of potassium oxalate. The large excess of

the potassium oxalate is to make sure of keeping the iron salts in solution. The action of mercuric chloride on an amalgam so prepared, for the purpose of adding more mercury to it, is far more rapid than the action on metallic silver, presumably because the amalgam is more finely divided. If a double (or mixed) chloride of silver and mercury contains metallic silver (an unattacked residue, for example), it will not give a constant weight at 100° , as metallic mercury is liberated by the silver and continuously volatilised.

The Amalgam AgHg.—In bulk, as dried over sulphuric acid without the aid of heat (in a steam-oven such an amalgam lost mercury at a rate equivalent to 0.47 per cent. per hour), this amalgam appears as a grey, non-adherent powder, which can be easily burnished into a metallic film. It consists of rounded particles, generally about 0.003 mm. in diameter. Some are oval and up to 0.005 mm. long, and others are as small as 0.002 mm. As diffused in cedarwood oil for microscopic examination, the particles have a marked tendency to adhere in rows, often branched, Y-shape, but the individual particles are quite distinct, and there is no appearance of a want of homogeneity. The silver mercurous chloride from which it was obtained was in similar rounded particles, but more varied in size, and on the whole rather smaller. These differences are probably accidental, and it seems almost certain that on the reduction of the chloride to the amalgam the separate particles retain their individuality. The specific gravity of the amalgam, taken in water at 20° and compared with water at 20° , was 12.8055. When pumping out the air, there appeared to be a continual evolution of gas, as if the amalgam decomposed the water. A second estimation with more stringent methods to remove air gave 12.8099. A determination in xylene showed that these figures are not low, and therefore that if the amalgam does act on the water the result is not sufficient to vitiate the determination. The calculated specific gravity, assuming no contraction when the two metals combine, is 12.29. Evidently, therefore, in the amalgam obtained as described, there is contraction on combination, but not nearly so much as in the crystalline amalgam which Joule obtained by placing mercury in silver nitrate solution. Such a preparation, which had approximately the same composition, had a specific gravity of 14.68, and another sample, obtained by adding more mercury and squeezing out as much as possible by a high pressure, gave 13.44. Other observers have found specific gravities for silver amalgams up to about 14.

The Amalgam AgHg₃.—When the amalgam AgHg is acted on by mercuric chloride, the resulting chloride (empirically AgHg_3Cl_4)

is not distinguishable when viewed in bulk from the double chloride AgHgCl_2 ; it is a white, soft-looking powder. When microscopically examined, it is at once clear that the characteristic structure of the double chloride, AgHgCl_2 , which persists in the amalgam AgHg , produced from it by reduction, has now gone—the particles are disintegrated. They are smaller, 0.001 mm. in diameter or less, and irregular in shape. This chloride is easily reduced, and the dried amalgam, AgHg_3 , appears in bulk as an adherent powder. If allowed to fall from the side of the bottle, it retains the shape of the bottle, much as undried sea-sand does. If rubbed with the side of a knife it crunches, and the bright metallic scale so produced appears, on magnification, to have globules of mercury exuding from it. If pushed up into a fold of wash-leather with a tooth-brush handle, a large proportion of clean mercury globules can be pressed through the leather. When stirred into cedarwood oil and examined microscopically, it appears as crumbling, coherent, homogeneous masses, not separable into individual grains. The masses have no appearance of liquidity, their outlines are irregular and angular, especially the smaller detached particles, and the points tend to be blunt rather than spiky.

It is not proposed to continue this investigation, but Dr. J. C. Philip hopes to examine the physical properties of some of these amalgams, and to study the influence of the medium on the velocity of the reaction between mercuric halides and metallic silver.

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XXXVIII.—*Halogen Derivatives of Malonanilide, Ethyl Malonanilate, and Malonanilic Acid.*

By FREDERICK DANIEL CHATTAWAY and FREDERICK ALFRED MASON.

COMPOUNDS of this nature are at present almost unknown, although a knowledge of their properties is necessary before the action of halogens on the parent substances can be followed and before one of the least studied cases of intramolecular rearrangement can be further investigated.

The scanty literature dealing with the subject leaves the impression that compounds of this class are difficult to prepare by a direct method, whereas the exact reverse is the case.

The halogen derivatives of malonanilide and of ethyl
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malonanilate are produced together when malonic ester in some excess is heated for a short time with the corresponding aniline, and can easily be separated, owing to the sparing solubility of the anilides in all ordinary solvents. The best results are obtained when about one gram-molecule of the aniline and one and a-half gram-molecules of malonic ester are employed; if less ester is used, some aniline, which is troublesome to remove by crystallisation, is left, whilst if more ester is taken, the products remain partly dissolved in the excess which has to be distilled off, a brownish-coloured product, which needs much purification, being obtained. About 10 to 15 grams of aniline is a convenient amount to use in one operation.

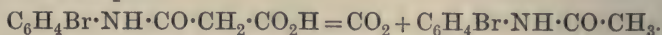
The aniline and ester are heated together in a flask attached to a long tube, which serves as a condenser, and the rate of boiling of the mixture is regulated so that the alcohol formed mainly escapes while the malonic ester is returned to the flask.

The yields are generally good, no appreciable decomposition occurring, the loss arising only from the necessary separation and purification.

The halogen-substituted malonanilic acids are also very easily obtained by hydrolysing the substituted malonanilic esters: the crude products from which the substituted malonanilides have been separated suffice for this purpose.

The esters can be hydrolysed by heating for a short time with aqueous sodium or potassium hydroxide, or even by heating for a longer time with water alone, but it is preferable to suspend them in a dilute solution of sodium carbonate and to pass steam through the liquid until the ester disappears. This method has the advantage that if any aniline remains admixed with the crude ester or is formed during hydrolysis, it passes over with the steam. The acid is separated from the sodium salt in a crystalline state, after concentrating the solution if necessary, by adding a slight excess of hydrochloric acid.

When heated, the malonanilic acids decompose quantitatively into carbon dioxide and the corresponding substituted acetanilide, thus, for example:



EXPERIMENTAL.

pp-Dichloromalonanilide, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Cl}$.

This compound, together with ethyl *p*-chloromalonanilate, is produced when *p*-chloroaniline is heated with ethyl malonate. A mixture of 12 grams of *p*-chloroaniline and 25 grams of ethyl

malonate was gently boiled for thirty minutes, the alcohol formed being allowed to escape. The semi-solid mass left on cooling was shaken with four times its bulk of alcohol, and the dichloromalonanilide which remained undissolved was collected and recrystallised alternately from alcohol and acetic acid. It is fairly soluble in boiling alcohol or acetic acid, and separates from either in small, slender, colourless needles, which, when dry, form a felted mass. The yield of pure product obtained thus is about 20 per cent. of the theoretical yield from the amount of aniline used.

pp-*Dichloromalonanilide* melts and decomposes at 261° :

0.2474 gave 0.2206 AgCl. Cl = 22.06.

$C_{15}H_{12}O_2N_2Cl_2$ requires Cl = 21.95 per cent.

Ethyl p-Chloromalonanilate, $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$.

This compound was obtained as a white, crystalline powder by slowly adding water to the filtrate from which dichloromalonanilide had been separated. It was purified by repeatedly crystallising it from hot alcohol, in which it is very easily soluble, and from which it separates in short, colourless prisms, melting at 97° . It is very readily soluble in all common organic solvents, but only very sparingly so in water:

0.2146 gave 0.1285 AgCl. Cl = 14.81.

$C_{11}H_{12}O_3NCl$ requires Cl = 14.68 per cent.

p-Chloromalonanilic Acid, $C_6H_4Cl \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

This compound was prepared by suspending ethyl *p*-chloromalonanilate in twenty times its weight of water containing rather more than the equivalent amount of sodium carbonate and passing steam through the liquid until the ester had disappeared. On adding hydrochloric acid in slight excess to the cooled product, the acid separated in thin, colourless plates. It was purified by recrystallisation either from hot water, in which it is moderately soluble, or from hot alcohol, in which it is readily so. It separates from either solvent in glistening, colourless, flattened prisms or plates. On heating, it melts and decomposes, and evolves carbon dioxide at about 168° ,* leaving a residue of pure *p*-chloroacetanilide, which, after solidification, re-melts at 175° :

* The melting points of this and the other substituted malonanilic acids described in the paper represent the temperatures at which the substances melt and rapidly decompose with gas evolution when quickly heated. The temperatures at which this melting takes place vary considerably with the rate of heating. Decomposition occurs to some extent before these temperatures are reached, and if the acids are slowly heated, they appear to melt at lower temperatures.

0.2123 gave 0.1439 AgCl. $\text{Cl} = 16.77$.

$\text{C}_9\text{H}_8\text{O}_3\text{NCl}$ requires $\text{Cl} = 16.61$ per cent.

2 : 4 : 2' : 4'-Tetrachloromalonanilide,
 $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_3\text{Cl}_2$.

This compound was obtained, together with ethyl 2 : 4-dichloromalonanilate, by boiling for about forty-five minutes a mixture of 16 grams of 2 : 4-dichloroaniline and 24 grams of ethyl malonate. The tetrachloromalonanilide was separated as described under the corresponding dichloro-compound, and purified by recrystallisation from boiling acetic acid. It is very sparingly soluble in boiling alcohol, and moderately so in boiling acetic acid. It crystallises in colourless, long, flattened needles or prisms, melting at 214° :

0.2558 gave 0.3748 AgCl. $\text{Cl} = 36.25$.

$\text{C}_{15}\text{H}_{10}\text{O}_2\text{N}_2\text{Cl}_4$ requires $\text{Cl} = 36.19$ per cent.

Ethyl 2 : 4-Dichloromalonanilate, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2 \cdot \text{C}_2\text{H}_5$.

This compound separated on cautiously adding water to the alcoholic filtrate from which the tetrachloromalonanilide had been separated. It was several times recrystallised alternately from boiling acetic acid and alcohol, in both of which it is readily soluble. It crystallises in colourless, flattened prisms, melting at 81° :

0.2527 gave 0.2620 AgCl. $\text{Cl} = 25.65$.

$\text{C}_{11}\text{H}_{11}\text{O}_3\text{NCl}_2$ requires $\text{Cl} = 25.69$ per cent.

2 : 4-Dichloromalonanilic Acid, $\text{C}_6\text{H}_3\text{Cl}_2 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$.

This compound was prepared exactly as described under *p*-chloromalonanilic acid. It is sparingly soluble in hot water, readily so in boiling alcohol, and crystallises from the latter in colourless, slender, flattened prisms. It melts and evolves carbon dioxide at about 164° , and leaves a residue of pure 2 : 4-dichloroacetanilide:

0.2896 gave 0.3337 AgCl. $\text{Cl} = 28.50$.

$\text{C}_9\text{H}_7\text{O}_3\text{NCl}_2$ requires $\text{Cl} = 28.60$ per cent.

2 : 4 : 6 : 2' : 4' : 6'-Hexachloromalonanilide,
 $\text{C}_6\text{H}_2\text{Cl}_3 \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NH} \cdot \text{C}_6\text{H}_2\text{Cl}_3$.

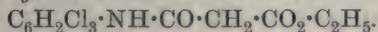
2 : 4 : 6 : 2' : 4' : 6'-Hexachloromalonanilide, together with ethyl 2 : 4 : 6-trichloromalonanilate, was prepared by gently boiling for an hour a mixture of 20 grams of 2 : 4 : 6-trichloroaniline and 40 grams of ethyl malonate, allowing the alcohol formed to escape. About 20 grams of unchanged malonic ester were then distilled

off. The residue was boiled with about 200 c.c. of alcohol, and the hexachloromalonanilide, which is practically insoluble in alcohol, was filtered off from the hot liquid. After washing repeatedly with boiling alcohol, the white, crystalline residue was several times crystallised from boiling acetic acid, in which it is sparingly soluble, and from which it crystallises in colourless, very slender, hair-like needles. It turns brown, melts, and evolves gas at about 306° :

0.1911 gave 0.3545 AgCl. $\text{Cl}=45.89$.

$\text{C}_{15}\text{H}_8\text{O}_2\text{N}_2\text{Cl}_6$ requires $\text{Cl}=46.17$ per cent.

Ethyl 2: 4: 6-Trichloromalonanilate,



This was obtained by adding water to the alcoholic filtrate from the hexachloromalonanilide and repeatedly crystallising the ester thus separated from boiling alcohol. It is easily soluble in hot alcohol, and crystallises in colourless, slender prisms, melting at 141° :

0.3361 gave 0.4643 AgCl. $\text{Cl}=34.17$.

$\text{C}_{11}\text{H}_{10}\text{O}_3\text{NCl}_3$ requires $\text{Cl}=34.26$ per cent.

2: 4: 6-Trichloromalonanilic Acid, $\text{C}_6\text{H}_2\text{Cl}_3\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.

This was prepared exactly as were the previously described acids. It was repeatedly crystallised from boiling alcohol, in which it is moderately easily soluble. It crystallises from alcohol in colourless, slender prisms, and from boiling water, in which it is sparingly soluble, in small, fine, colourless needles. When heated, it melts and evolves carbon dioxide at about 172° , forming 2: 4: 6-trichloroacetanilide:

0.1643 gave 0.2495 AgCl. $\text{Cl}=37.57$.

$\text{C}_9\text{H}_6\text{O}_3\text{NCl}_3$ requires $\text{Cl}=37.66$ per cent.

pp-Dibromomalonanilide, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Br}$.

Each bromine compound was prepared and isolated in a manner resembling that described under the corresponding chlorine compound, so that it is only necessary to record their distinctive peculiarities.

pp-Dibromomalonanilide is sparingly soluble in boiling alcohol, and moderately so in hot acetic acid. It crystallises from either solvent in colourless, slender needles, melting at 268° . If kept at this temperature, some decomposition takes place, the fused substance turning brown and giving off bubbles of gas. The other halogen-substituted malonanilides behave similarly:

0.2865 gave 0.2598 AgBr. $\text{Br}=38.59$.

$\text{C}_{15}\text{H}_{12}\text{O}_2\text{N}_2\text{Br}_2$ requires $\text{Br}=38.80$ per cent.

Ethyl p-Bromomalonanilate, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$.

Ethyl *p*-bromomalonanilate crystallises from alcohol, in which it is easily soluble, in colourless, short, rhombic prisms, melting at 99° : 0.2715 gave 0.1788 AgBr. Br=28.03.

$C_{11}H_{12}O_3NBr$ requires Br=27.94 per cent.

p-Bromomalonanilic Acid, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

This compound is sparingly soluble in boiling water, but readily so in hot alcohol. It crystallises from water or alcohol in colourless, flattened, slender prisms. It melts at 169° , carbon dioxide is evolved, and *p*-bromoacetanilide is formed:

0.1750 gave 0.1271 AgBr. Br=30.91.

$C_9H_8O_3NBr$ requires Br=30.98 per cent.

2: 4: 2': 4'-*Tetrabromomalonanilide*,

$C_6H_3Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_3Br_2$.

This compound crystallises from boiling acetic acid, in which it is moderately soluble, in colourless, long, flattened needles or prisms, melting at 233° :

0.2092 gave 0.2769 AgBr. Br=56.33.

$C_{15}H_{10}O_2N_2Br_4$ requires Br=56.11 per cent.

Ethyl 2: 4-Dibromomalonanilate,

$C_6H_3Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2 \cdot C_2H_5$.

This compound crystallises from alcohol, in which it is easily soluble, in colourless, slender, flattened prisms, melting at 86° :

0.2431 gave 0.2496 AgBr. Br=43.69.

$C_{11}H_{11}O_3NBr_2$ requires Br=43.80 per cent.

2: 4-Dibromomalonanilic Acid, $C_6H_3Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

2: 4-Dibromomalonanilic acid is sparingly soluble in water, but easily so in alcohol. It crystallises from alcohol in colourless, flattened prisms. When heated, it melts, and evolves carbon dioxide at 174° , 2: 4-dibromoacetanilide being formed:

0.2880 gave 0.3195 AgBr. Br=47.21.

$C_9H_7O_3NBr_2$ requires Br=47.44 per cent.

2: 4: 6: 2': 4': 6'-*Hexabromomalonanilide*,

$C_6H_2Br_3 \cdot NH \cdot CO \cdot CH_2 \cdot CO \cdot NH \cdot C_6H_2Br_3$.

This anilide is so sparingly soluble in all ordinary solvents that it can only be recrystallised in very small amount from boiling acetic acid. A few tenths of a gram only are dissolved by a litre

of boiling acetic acid. It separates from this solvent in colourless, very small, hair-like needles. It can be recrystallised from boiling nitrobenzene, but the product obtained is not quite pure, and very considerable loss from decomposition occurs. It melts and evolves gas at 331° :

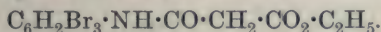
0.1314 gave 0.2041 AgBr. Br = 66.10.

$C_{15}H_8O_2N_2Br_6$ requires Br = 65.90 per cent.

Freund (*Ber.*, 1884, 17, 782) obtained a compound to which he assigned this constitution by dissolving malonanilide in glacial acetic acid, and adding bromine in slight excess to the warmed solution drop by drop. The liquid on cooling deposited a thick crop of needles, which, after several recrystallisations from acetic acid, melted at $145-146^{\circ}$. This substance, on heating in a sealed tube with fuming hydrochloric acid at 200° , yielded a compound which he regarded as symmetrical tribromoaniline, and from this observation he deduced its constitution.

Freund's compound, however, differs so entirely in its properties from the compound described above, which itself possesses all the properties that would be expected from a consideration of those of the other members of the class described in this paper, that it cannot have the constitution assigned by him to it.

Ethyl 2:4:6-Tribromomalonanilate,



Ethyl 2:4:6-tribromomalonanilate is readily soluble in hot alcohol, and crystallises from it in colourless, slender prisms, melting at 177° :

0.1458 gave 0.1854 AgBr. Br = 54.11.

$C_{11}H_{10}O_3NBr_3$ requires Br = 54.02 per cent.

2:4:6-Tribromomalonanilic Acid, $C_6H_2Br_3 \cdot NH \cdot CO \cdot CH_2 \cdot CO_2H$.

2:4:6-Tribromomalonanilic acid crystallises from alcohol, in which it is moderately soluble, in small, colourless needles. If the acid is rapidly heated, it melts and evolves carbon dioxide at about 201° , 2:4:6-tribromoacetanilide being produced. If slowly heated, however, it decomposes below this temperature without melting, carbon dioxide as before is given off, whilst 2:4:6-tribromoacetanilide, which, if the temperature be raised, melts sharply at 232° , is left in the tube:

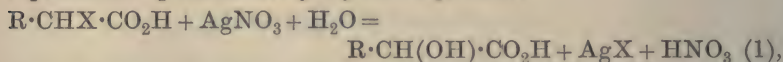
0.2000 gave 0.2699 AgBr. Br = 57.43.

$C_9H_6O_3NBr_3$ requires Br = 57.66 per cent.

XXXIX.—*Reactivity of the Halogens in Organic Compounds. Part IV. Interaction of Bromoacetic, α -Bromopropionic, and α -Bromobutyric Acids and their Sodium Salts with Silver Salts in Aqueous Solution. Catalytic Action of Silver Halides.*

By GEORGE SENTER.

IN previous papers (Trans., 1907, **91**, 460; Proc., 1908, **24**, 89; *Arrhenius Jubelband*, 1910, II, 511; Trans., 1909, **95**, 1827) the results of an experimental investigation of the rate of displacement of the halogens in the lower members of the series of halogen-substituted fatty acids have been communicated, and the mechanism of the respective reactions has been discussed. The present paper deals mainly with the interaction of the first three members of the series of α -bromo-fatty acids and their sodium salts with silver nitrate and silver acetate in dilute aqueous solution. It was shown many years ago by Beckurts and Oddo (*Ber.*, 1881, **14**, 576; 1885, **18**, 222) that the reaction between silver nitrate and the lower members of the series of bromo-fatty acids in aqueous solution is represented quantitatively by the equation:



in which R represents hydrogen or an alkyl group, and X a halogen atom.

In the course of the present investigations, the remarkable observation was made that reactions of the above type are very markedly accelerated by silver bromide; even when the solution is only 1/300 molar with reference to silver bromide (which is, of course, mainly present in the insoluble form), the rate of the reaction may be doubled or even trebled. This action appears to account for a number of hitherto unexplained observations made by previous investigators.

The other more important results of the investigation are that the rate of reaction increases very considerably with the increase in complexity of the alkyl group R, and that the sodium salts react more rapidly than the free acids. Nitric acid exerts a very powerful retarding effect on the reactions in which silver nitrate is concerned. Silver acetate reacts with the bromo-fatty acids more rapidly than does silver nitrate under equivalent conditions.

EXPERIMENTAL.

Method of Measurement.—The reacting substances were mixed at constant temperature in small tubes of Jena glass, which were then corked and kept in a thermostat at a temperature kept constant to within 0.1° . At definite intervals the contents of a tube were poured into a slight excess of a $N/50$ -solution of ammonium thiocyanate, which at once stopped the reaction, 5 c.c. of a concentrated solution of iron alum and 5 c.c. of concentrated nitric acid, free from nitrous fumes, were then added, and the excess of thiocyanate estimated by titrating with $N/50$ -silver nitrate.

It is known that the above method of titration does not give accurate results for chlorides, owing to the solubility of the precipitated silver chloride in ammonium thiocyanate. Theoretically, however, there should be no appreciable error in the case of bromides, owing to the much smaller solubility of silver bromide, and this conclusion has been confirmed experimentally by Rosanoff and Hill (*J. Amer. Chem. Soc.*, 1907, **29**, 1467). In order to ensure that no error arises in the present case owing to the presence of precipitated silver bromide, the method of titration described above has been tested in various ways, and has been found to give quite accurate results.

The tubes in which the reactions were carried out held about 15 c.c., and in all cases the reaction mixture measured 12 c.c. The titration values quoted in the tables are throughout (except in table I) the mean of two simultaneous experiments. The measurements were made at 26.0° .

Reaction between α -Bromopropionic Acid and Silver Nitrate.

The results of a typical series of experiments with α -bromopropionic acid and silver nitrate are quoted in table I. The unit of concentration is the amount of silver nitrate contained in 1 c.c. of a $N/50$ -solution of the salt, and the concentration of the halogen-fatty acids (and their sodium salts) is expressed in equivalent units, in accordance with the experimental fact that $R\cdot CHBr\cdot CO_2H$ (and $R\cdot CHBr\cdot CO_2Na$) is equivalent to $AgNO_3$. The constants in the last column are calculated according to the equation for a reaction of the second order:

$$k = \frac{1}{t} \cdot \frac{x}{a(a-x)}$$

when the reacting substances are present in equivalent amounts. In all cases, $a-x$ in the tables represents the concentration of the

silver nitrate at the time t , as this is the substance which is actually estimated.

If it is desired to refer k , the velocity-coefficient or velocity constant of the reaction, to a concentration of 1 mol. per litre, the values of k given in the tables must be multiplied by $12 \times 50 = 600$, since the values quoted are obtained by titrating 12 c.c. of the reaction mixture with 1/50 molar thiocyanate.

Throughout this paper, the concentrations given refer to the reaction mixture; thus, in the experiments quoted in table I, the reaction mixture was initially $N/30$ with reference to both the reacting substances.

TABLE I.

Silver nitrate, $N/30$. α -Bromopropionic acid, $N/30$.

t (min.).	$a - x$.	k .	$a - x$.	k .
0	20.0	—	20.0	—
10	18.1	0.00050	18.0	0.00056
30	14.7	0.00060	14.7	0.00060
90	10.2	0.00058	10.0	0.00056

These figures show that the results of parallel experiments are in good agreement, and the fair agreement of the velocity-coefficients in the course of a reaction is in accord with the assumption that the reaction is bimolecular. It will be shown in the sequel, however, that the latter result is only attained owing to a combination of two factors which influence the reaction in opposite directions.

It is well known that one of the best methods of deciding the "order" of a reaction is to measure its velocity with varying initial concentrations; in this way disturbances arising in the course of the reaction are to a great extent eliminated. The results for the reaction under discussion are given in table II, the values of k , when the concentrations are not equivalent, being calculated by the general formula for a bimolecular reaction:

$$0.4343 k = \frac{1}{t(a-b)} \log_{10} \frac{b(a-x)}{a(b-x)},$$

where the symbols have the usual significance.

TABLE II.

Concentration of silver nitrate.	Concentration of bromopropionic acid.	k .
$N/10$	$N/40$	0.00047
$N/20$	$N/40$	0.00059
$N/40$	$N/40$	0.00054
$N/20$	$N/20$	0.00053
$N/20$	$N/10$	0.00051

The above results appear to show that, in spite of certain irregularities, the rate of the reaction is in the first instance

proportional to the initial concentration of the reacting substances through a range of concentration from $N/10$ to $N/40$ in each case.

It was soon noticed that when the aqueous solution of the acid was not freshly prepared, the reaction was considerably more rapid. This is illustrated by the results quoted in the accompanying table.

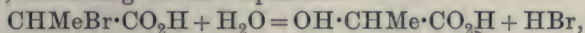
TABLE III.

Silver nitrate and bromopropionic acid, each $N/30$.

(Acid solution, two hours old.)			(Acid solution, kept two days at 26°.)		
t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .
0	20.0	—	0	20.0	—
10	18.5	0.00041	10	16.4	0.00110
30	15.4	0.00050	30	12.0	0.00111
90	10.5	0.00050	90	8.3	0.00080

It is clear that the initial velocity is nearly three times as great when the acid solution is kept two days before the rate of reaction is measured.

It is well known that α -bromopropionic acid is slowly decomposed by water, according to the equation:



and in an earlier paper the results of an experimental investigation of this reaction have been communicated. A little hydrobromic acid is formed during the reaction, and at once reacts with part of the silver nitrate on mixing the reacting substances. As the speed of the reaction is deduced from the rate at which the silver nitrate is used up, the apparent speed in the presence of hydrobromic acid will be greater than the actual speed with which silver nitrate and α -bromopropionic acid react. In order to estimate the error thus caused, the rate of hydrolytic decomposition of bromopropionic acid at 26° has been measured at 26° with the following results (table IV). The concentrations of bromopropionic acid and of hydrobromic acid are expressed in terms of the number of c.c. of $N/20$ -sodium hydroxide required to neutralise 5 c.c. of the solution, which was approximately $N/5$:

TABLE IV.

Time (days).	Five c.c. of acid solution titrated.	Concentration of HBr formed.	
		In c.c. of $N/20$ -NaOH.	Normality.
0	19.70	0.00	—
3	20.10	0.40	0.001
6	20.35	0.65	0.0016
9	20.60	0.90	0.0023
12	20.80	1.10	0.0028

The reaction at 26° is therefore extremely slow, and the amount

of hydrobromic acid formed is much too small to account directly for the results given in table III.

There would appear to be at least two plausible explanations of the results in question: (1) that the silver bromide formed in the course of the reaction exerts a catalytic influence; (2) that the bromopropionic acid in aqueous solution undergoes a slow change into a second more active modification. The first suggestion can at once be tested by adding some hydrobromic acid or potassium bromide to the bromopropionic acid before adding the silver nitrate. Some of the results obtained in this way are given in table V.

TABLE V.

<i>Composition of Mixture I.</i>			<i>Composition of Mixture II.</i>		
Bromopropionic acid, $N/5$...	2 c.c.		Bromopropionic acid, $N/5$...	2 c.c.	
Water	5 "		Potassium bromide, $N/25$	2 "	
Silver nitrate, $N/12.5$	5 "		Water	2 "	
			Silver nitrate, $N/12.5$	6 "	
t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .
0	20.0	—	0	20.0	—
10	18.5	0.00041	10	15.7	0.00137
30	15.4	0.00050	20	13.3	0.00126
90	10.5	0.00050	40	10.0	0.00125

The data in the above table show that, after mixing, the two solutions are exactly equivalent in concentration; the only difference is that in the second mixture a small amount of silver bromide (and potassium nitrate) is present. The mixture is only $1/150$ molar with respect to this salt, and doubtless the greater part of it is present in the insoluble form, yet the remarkable result is obtained that this trace of silver bromide more than trebles the initial speed of the main reaction. Moreover, this by no means represents the maximum catalytic power of the silver bromide, as the greater part of it coagulates and rises to the top of the solution soon after mixing the reagents.

Reference to the data in table III shows that the solution of bromopropionic acid, which had stood two days at 26° , cannot have been more than $1/1000$ normal with reference to hydrobromic acid, so that the small amount of silver bromide formed by interaction of the acid with silver nitrate has a very powerful catalytic action.

The catalytic acceleration of reactions of this type by silver bromide and iodide is further referred to in a later part of the paper (pp. 357, 358).

Effect of Acids and of Sodium Nitrate on the Reaction Velocity.

(a) *Nitric Acid*.—Nitric acid, even in very dilute solution, very markedly retards the reaction between silver nitrate and α -bromopropionic acid. Some of the results, typical of an extended series of experiments on this point, are given in the accompanying table.

TABLE VI.

Silver nitrate, $N/20$. Bromopropionic acid, $N/20$.

No nitric acid.			Nitric acid, $N/30$.			Nitric acid, $N/15$.		
t .	$a-x$.	k .	t .	$a-x$.	k .	t .	$a-x$.	k .
0	30.0	—	0	30.0	—	0	30.0	—
10	26.7	0.00041	20	28.0	0.000120	30	28.45	0.000060
30	21.5	0.00045	60	25.0	0.000111	90	25.75	0.000062

The figures show that in the presence of $N/15$ -nitric acid the rate of the reaction is diminished to about $1/7$ th of its original value.

(b) *Benzenesulphonic Acid*.—For comparison with nitric acid, some experiments were made with benzenesulphonic acid under the same conditions. It was found that the latter acid retards the reaction to a rather greater extent than nitric acid. The initial value of the constant in the presence of $N/15$ -benzenesulphonic acid is 0.000053, as compared with 0.000061 for $N/15$ -nitric acid.

It is probable that benzenesulphonic acid is a rather stronger acid than nitric acid, but the difference in the reactivities seems rather greater than can be accounted for on this basis.

(c) *Lactic Acid*.—As lactic acid is one of the products of the reaction, its influence on the velocity was measured with the following results:

TABLE VII.

Silver nitrate, $N/20$. Bromopropionic acid, $N/20$.

No lactic acid.			Lactic acid, $N/5$.		
t (min.).	$a-x$.	k .	t (min.).	$a-x$.	k .
0	30.0	—	0	30.0	—
10	26.1	0.00050	10	26.9	0.00038
30	20.4	0.00053	30	22.1	0.00040
60	14.9	0.00056	60	18.4	0.00036

(d) *Sodium Nitrate*.—The results of a series of observations with this salt are given in the accompanying table; much higher concentrations were used than in the case of the acids:

TABLE VIII.

Silver nitrate, *N*/30. Bromopropionic acid, *N*/30.

<i>t</i> (min.).	No sodium nitrate.		Sodium nitrate, <i>m</i> /2.		Sodium nitrate, <i>m</i> /1.	
	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	20.0	—	20.0	—
10	17.9	0.00060	18.3	0.00045	18.7	0.00035
30	14.6	0.00062	15.7	0.00045	16.2	0.00039

The facts that nitric acid and benzenesulphonic acid, which are both highly ionised in solution, retard the reaction to about the same extent, and that the NO_3' ion has only a very slight retarding action, indicate that the effect in question is mainly due to the H^+ ions. This is confirmed by the fact that lactic acid, which is a comparatively weak acid, has a very slight retarding action. The bearing of these results on the mechanism of the reaction is discussed later (p. 361).

Effect of Alcohol and of Acetone on the Rate of Reaction.

A few experiments were made in which half the water used as solvent was displaced by alcohol and by acetone respectively; the results were as follows:

TABLE IX.

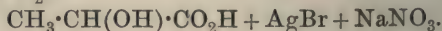
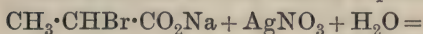
Silver nitrate, *N*/30. Bromopropionic acid, *N*/30.

<i>t</i> (min.).	Solvent... Water.		Water + alcohol.		Water + acetone.	
	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	20.0	—	20.0	—
10	18.0	0.00056	17.5	0.00071	17.4	0.00073
30	14.6	0.00062	13.9	0.00073	14.3	0.00067

It is interesting to note how small an alteration is produced in the reaction velocity by the displacement of half the water by alcohol or by acetone. It has already been shown by Euler (*Ber.*, 1906, **39**, 2726) that the rate of reaction between chloroacetic acid and silver nitrate is approximately the same in water and in 45 per cent. alcohol.

Sodium Bromopropionate and Silver Nitrate.

The reaction in this case is represented by the equation:



The sodium bromopropionate was prepared just before the reaction by careful neutralisation of a solution of bromopropionic acid with sodium hydroxide. The results of one series of experi-

ments, in which the relative activities of the acid and its sodium salt are compared, are given in the accompanying table:

TABLE X.

Silver nitrate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /30.			Silver nitrate, <i>N</i> /30. Sodium bromopropionate, <i>N</i> /30.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
10	18.0	0.00056	5	16.6	0.0020
30	14.7	0.00060	15	11.0	0.0027
90	10.2	0.00054	45	6.4	0.0024

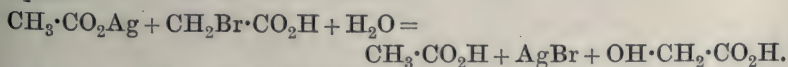
The velocity-coefficients, k_1 , for a bimolecular reaction in the case of the sodium salt are only in moderate agreement, a result which is doubtless to be anticipated. The initial velocity is about four times that obtained for the free acid. The considerable increase of the coefficient between five and fifteen minutes is no doubt due to the catalytic influence of silver bromide. A few measurements were also made to determine the influence of the initial concentration on the reaction velocity, with the following results:

	<i>k</i> .
Sodium bromopropionate, <i>N</i> /30	} 0.0020
Silver nitrate, <i>N</i> /30	
Sodium bromopropionate, <i>N</i> /60	} 0.0030
Silver nitrate, <i>N</i> /60	

showing that the initial velocity is the greater the more dilute the solution.

Bromopropionic Acid and Silver Acetate.

If the conclusion drawn from the experiments already described—that silver bromide exerts a catalytic influence on the rate of reaction—is valid, the velocity-coefficients calculated for a reaction of the second order ought regularly to increase, owing to the increase in the amount of silver bromide as the reaction proceeds. However, nitric acid, another product of the reaction, exerts a retarding influence, and the result of these two effects is that in many cases the reactions follow the law for a bimolecular reaction fairly accurately. In order to eliminate the retarding influence of nitric acid, it was considered desirable to perform a few experiments with the silver salt of a weak acid, and for this purpose silver acetate was chosen. The reaction in this case is represented by the equation:



Some typical results are quoted in table XI:

TABLE XI.

Fresh Bromopropionic Acid.

Silver acetate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /30.			Silver acetate, <i>N</i> /100. Bromopropionic acid, <i>N</i> /30.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	6.0	—
5	18.2	0.00100	10	4.75	0.00130
15	14.0	0.00143	30	2.75	0.00148
30	9.5	0.00186	60	0.70	0.00186

Bromopropionic Acid (kept two days at 26°).

Silver acetate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /30.			Silver acetate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /60.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
5	16.8	0.00200	10	16.5	0.00250
15	10.5	0.00307	30	12.8	0.00327
30	7.6	(0.00272)			

It will be observed that in all these experiments the velocity-coefficients calculated for a reaction of the second order increase very considerably during the reaction, doubtless owing to the catalytic influence of the silver bromide. The same effect is seen in the solution which has been kept two days, and in which, therefore, a little hydrobromic acid has been formed. The very small amount of silver bromide produced as soon as the two solutions are mixed is sufficient to double the initial speed of the reaction. This catalytic effect is also illustrated in the following table; in one case a small amount of potassium bromide is added to the acid before mixing:

TABLE XII.

Silver acetate, <i>N</i> /25	8 c.c.	Silver acetate, <i>N</i> /25	9 c.c.		
Bromopropionic acid, <i>N</i> /6.25 .	2 „	Bromopropionic acid, <i>N</i> /6.25 .	2 „		
Water	2 „	Potassium bromide, <i>N</i> /25.....	1 „		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	16.00	—	0	16.00	—
5	14.20	0.00158	5	11.30	0.00520
10	12.40	0.00181	10	9.80	0.00395
20	9.65	0.00206	20	7.00	0.00402
30	7.00	0.00263			

These results indicate that 1/300 molar silver bromide more than trebles the initial speed of the reaction, but that the velocity falls off somewhat as the reaction proceeds. This is doubtless connected with the fact that the greater part of the silver bromide soon coagulates, and rises to the top of the solution; it can then exert no catalytic influence.

Relative Velocities with Silver Nitrate and Silver Acetate.—

Simultaneous measurements were made with silver nitrate and silver acetate in equivalent concentration, in order to obtain an accurate record of their relative activities with bromopropionic acid. The results are as follows:

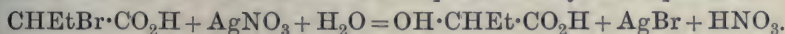
TABLE XIII.

Silver nitrate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /30.			Silver acetate, <i>N</i> /30. Bromopropionic acid, <i>N</i> /30.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
10	17.8	0.00062	5	17.9	0.00120
30	14.2	0.00068	17	12.6	0.00170
90	9.5	0.00061	45	6.6	0.00220

It follows that the initial velocity with the nitrate is about half that with the acetate under corresponding conditions. The bearing of this result on the mechanism of the reaction is considered later.

Reaction between α-Bromobutyric Acid and Silver Nitrate.

Corresponding measurements to those just described for bromopropionic acid have been made with bromobutyric acid, but not in the same detail. The reaction is represented by the equation:



The results are similar to those obtained for bromopropionic acid, except that the velocity-coefficients diminish more rapidly during the reaction. The data for experiments in which the initial concentrations were varied are given in table XIV, the initial values of the velocity-coefficients being given in the third column:

TABLE XIV.

Concentration of silver nitrate.	Concentration of bromobutyric acid.	<i>k</i> .
<i>N</i> /60	<i>N</i> /60	0.0060
<i>N</i> /40	<i>N</i> /40	0.0034
<i>N</i> /20	<i>N</i> /40	0.0021
<i>N</i> /10	<i>N</i> /40	0.0014
<i>N</i> /40	<i>N</i> /20	0.0034
<i>N</i> /40	<i>N</i> /10	0.0028

It is clear from these results that when the concentration of silver nitrate is kept constant, and that of the bromopropionic acid varied, there is not much alteration in the magnitude of the velocity-coefficients; in other words, the rate of the reaction is approximately proportional to the concentration of the bromobutyric acid. On the other hand, the coefficients diminish considerably as the initial concentration of silver nitrate is increased, which indicates that when the silver nitrate concentration is increased, the rate of the reaction does not increase in the same proportion. This does not correspond with the behaviour of silver

nitrate and α -bromopropionic acid, where the velocity-coefficients retain approximately the same value with varying concentration (p. 348).

Effect of Nitric Acid.—The actual observations are quoted in this case, as they illustrate very clearly the falling off in the magnitude of the velocity-coefficients as the reaction progresses:

TABLE XV.

Silver nitrate, $N/20$. Bromobutyric acid, $N/20$.

No nitric acid.			Nitric acid, $N/15$.			Nitric acid, $N/7.5$.		
t (min.).	$\alpha - x$.	k .	t (min.).	$\alpha - x$.	k .	t (min.).	$\alpha - x$.	k .
0	30.0	—	0	30.0	—	0	30.0	—
5	23.4	0.0019	15	24.6	0.00048	30	25.3	0.00020
15	18.8	0.0013	45	21.5	0.00029	90	22.6	0.00012

These results show that the retarding effect of nitric acid is considerable, and is approximately proportional to the concentration of the acid.

Sodium Bromobutyrate and Silver Nitrate.—The magnitude of the constant in $1/30$ molar solution of each of the reacting substances is 0.0060. The speed is therefore about 2.5 times that with the free acid, for which the constant is about 0.0024.

Bromoacetic Acid and Silver Nitrate.

As this reaction has already been investigated to some extent by Euler (*loc. cit.*), it has been considered sufficient for the present purpose to make a few measurements with the object of comparing this acid with the two higher acids as regards its reactivity with silver nitrate, and, further, to determine if this reaction, like the others, is catalytically accelerated by silver bromide. The results are given in table XVI:

TABLE XVI.

Silver nitrate, <i>N</i> /12.5	5 c.c.	Silver nitrate, <i>N</i> /12.5	6 c.c.		
Bromoacetic acid, <i>N</i> /5	2 „	Bromoacetic acid, <i>N</i> /5	2 „		
Water	5 „	Potassium bromide, <i>N</i> /25.....	2 „		
		Water	2 „		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
240	19.5	0.0000048	180	18.1	0.000029
1200	17.6	0.0000057	1200	11.6	0.000030
2760	13.4	0.0000089	2760	9.6	0.000022

The data quoted in the table show that the rate of reaction between silver nitrate and bromoacetic acid is very slow at 26° , the rate is only about $1/100$ th of the corresponding reaction with bromopropionic acid. Further, silver bromide greatly accelerates

the reaction—in a solution 1/150 molar with respect to this salt, the initial velocity is about six times that in the absence of the silver bromide.

Sodium Bromoacetate and Silver Nitrate.—The results given in table XVII show that sodium bromoacetate reacts with silver nitrate about three times as rapidly as does the free acid.

TABLE XVII.

Bromoacetic acid, <i>N</i> /30. Silver nitrate, <i>N</i> /30.			Sodium bromoacetate, <i>N</i> /30. Silver nitrate, <i>N</i> /30.		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	20.0	—	0	20.0	—
240	19.5	0.0000054	240	18.6	0.000016
1200	17.2	0.0000068	1200	13.2	0.000021
2760	13.8	0.0000081	2760	7.4	0.000031

Methyl Iodide and Silver Nitrate.

As this reaction has been measured by several previous observers, who, however, did not detect the catalytic influence of the silver iodide, it has been considered desirable to repeat the measurements, with special reference to the effect of silver iodide in aqueous solution. Some typical results are given in the accompanying table:

TABLE XVIII.

Solvent: Water.

I.			II.		
Silver nitrate, <i>N</i> /20... .. 5 c.c.			Silver nitrate, <i>N</i> /20 6 c.c.		
Methyl iodide, <i>N</i> /20 5 „			Methyl iodide, <i>N</i> /20 5 „		
Water..... 2 „			Potassium iodide, <i>N</i> /20..... 1 „		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	12.50	—	0	12.50	—
15	11.60	0.00042	15	10.70	0.00080
30	10.95	0.00039	30	9.65	0.00076
60	9.70	0.00039	60	8.00	0.00075
120	8.30	0.00034	120	6.70	0.00058
180	6.80	0.00037	180	5.10	0.00035

Solvent: Alcohol.

III (composition as I).			IV (composition as II).		
<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .	<i>t</i> (min.).	<i>a</i> - <i>x</i> .	<i>k</i> .
0	12.5	—	0	12.5	—
10	10.75	0.00130	10	10.4	0.00162
30	8.50	0.00126	30	8.3	0.00135
60	6.73	0.00116	60	6.4	0.00127
120	4.90	0.00104	120	4.5	0.00119

These results show that the reaction in aqueous solution is considerably accelerated by *N*/240-silver iodide, and there appears to

be a corresponding, but much smaller, acceleration in alcoholic solution. The latter result, however, is of a preliminary nature, as only one series of measurements was made in alcohol.

In all these cases it has to be remembered that the amount of silver iodide distributed through the solution is only a small fraction of the total amount, as the precipitate, especially in alcoholic solution, soon coagulates, and then rises to the top or sinks to the bottom of the solution, being thus to a great extent removed from the sphere of action.

In experiments III and IV, besides silver iodide, a little potassium nitrate (1/240 molar) is formed on mixing the solutions. Direct experiment shows, however, that even in 1/20 molar solution potassium nitrate exerts no appreciable influence on the rate of the reaction in aqueous solution, and the same may safely be assumed as to its effect in alcoholic solution in so small concentration.

According to the above table, the rate in ethyl alcohol is to the rate in water as 3: 1, a result not in satisfactory agreement with the recent measurements of Burke and Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 148), who find the ratio to be about 6: 1.

DISCUSSION OF RESULTS.

(1) *The Catalytic Influence of Silver Halogen Salts.*—In the previous pages it has been shown that silver bromide and silver iodide, even in extremely small concentration, exert a marked accelerating effect on reactions in which silver salts and halogen compounds are concerned. The conclusions drawn by previous observers as to the mechanism of such reactions require revision in the light of this observation.

The magnitude of the effect under favourable conditions is shown by the fact that 1/1000 molar silver bromide (about 0.002 gram in 12 c.c. of the reaction mixture) doubles the initial rate of reaction between silver nitrate and bromopropionic acid. Unfortunately, an accurate investigation of this effect is rendered very difficult by the fact already mentioned, that the precipitate soon coagulates and is withdrawn from the sphere of action by rising to the top or sinking to the bottom of the solution.

In order to find whether the catalytic influence pertained to the halogen compound in all forms, about 0.1 gram of freshly precipitated and carefully washed silver iodide was added to a mixture of silver nitrate and methyl iodide, and the rate of the reaction measured. The mean value of the velocity-coefficient in the presence of the added iodide was 0.00041, in its absence 0.00035, a comparatively small acceleration. The data quoted in table

XVIII show that $1/8$ th of this amount of iodide, precipitated in the reaction mixture, produces a much greater acceleration.

It seems probable, therefore, that the catalytic power is connected with the fineness of division of the silver iodide, possibly with its occurrence in the colloidal (hydrosol) form. Lottermoser and Rothe (*Zeitsch. physikal. Chem.*, 1908, **62**, 359) have shown that silver iodide hydrosol is much less stable when the silver nitrate is in excess than when excess of potassium iodide is present. As the silver salt is necessarily in excess in the reactions now under investigation, the comparatively rapid coagulation of the precipitate is accounted for. The view that the acceleration is connected with the colloidal form of the silver iodide appears to be supported by the observation that the catalytic effect is much smaller in alcoholic solution, in which the hydrosol appears to be less stable.

These observations are interesting also in connexion with the experiments of Miss Burke and Donnan on the reaction between the alkyl halides and silver nitrate in alcoholic solution. They found that whilst the velocity-coefficients calculated for a reaction of the second order remained more or less constant with variation of the initial concentration of the alkyl iodide, they increased with increasing concentration of the silver nitrate. In other words, if we consider a reaction-mixture originally $N/20$ with regard to both components, at the moment when the concentration has fallen to $N/40$, the reaction is found to be proceeding more rapidly than in a solution in which the reacting substances are originally $N/40$. In spite of a very detailed investigation, the results of which have just been published (*Zeitsch. physikal. Chem.*, 1909, **69**, 148), the authors have obtained no satisfactory explanation of this phenomenon, although they favour the suggestion of Wegscheider and Frankl (*Monatsh.*, 1907, **28**, 91) that it is the non-ionised silver nitrate which enters into reaction.

It is evident, however, that the results could be at once accounted for if silver iodide exerts a catalytic action in alcoholic solution, as it has been proved to do in aqueous solution in the present paper. The experiments in alcoholic solution quoted in table XVIII are, as already mentioned, of a preliminary character, and the matter is now being further investigated by Miss Burke. If the above explanation proves tenable, there will no longer be any experimental justification for Wegscheider's suggestion (*loc. cit.*) that it is the non-ionised silver nitrate which reacts.

(2) *The Mechanism of the Reactions.*—The mechanism of these reactions appears to be rather complicated, and the full discussion is postponed until the results of further investigations are available, more particularly the rate of reaction of the halogen-substituted

esters with silver nitrate in alcoholic solution. It will be sufficient for our present purpose to summarise the more important results communicated in this paper which have a bearing on the mechanism of the reactions. Reactions of this type have often been discussed by previous observers, but no very definite conclusions as to their mechanism have been drawn. All that can be said with certainty is that the relatively great velocity is conditioned in some way by the tendency to formation of the halogen silver salts (compare Euler, *Ber.*, 1906, **39**, 2726; Wegscheider, *Monatsh.*, 1907, **28**, 79). In this connexion it is interesting to note that definite compounds of silver nitrate with certain organic halogen compounds (for example, $\text{AgNO}_3 \cdot \text{CH}_2\text{I} \cdot \text{CN}$ and $\text{AgNO}_3 \cdot \text{CH}_2\text{I}_2$) have been prepared by Scholl and Steinkopf (*Ber.*, 1906, **39**, 4393).

The fact that silver bromide and iodide exerts a catalytic effect on the reactions renders the interpretation of the results somewhat difficult, as we are not entitled to assume that the observed velocities are proportional to the intrinsic velocities. Pending further investigation, however, it may be assumed that the nearest approach to the relative intrinsic velocities is obtained by taking the initial velocities of the respective reactions.

It has already been pointed out that as regards compounds of the type $\text{R} \cdot \text{CHBr} \cdot \text{CO}_2\text{H}$ and their sodium salts, the velocity increases greatly with the complexity of the substituting group R. Under corresponding conditions, the relative reactivities of the first three acids and their sodium salts with silver nitrate are as follows:

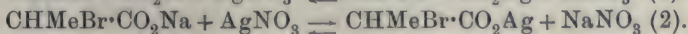
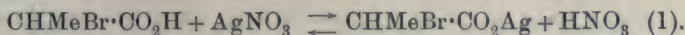
$\text{CH}_2\text{Br} \cdot \text{CO}_2\text{H}$ 0.0000055 [1]	$\text{CHMeBr} \cdot \text{CO}_2\text{H}$ 0.00055 [100]	$\text{CHEtBr} \cdot \text{CO}_2\text{H}$ 0.0025 [450]
$\text{CH}_2\text{Br} \cdot \text{CO}_2\text{Na}$ 0.000016 [4]	$\text{CHMeBr} \cdot \text{CO}_2\text{Na}$ 0.0025 [450]	$\text{CHEtBr} \cdot \text{CO}_2\text{Na}$ 0.0060 [1100]

The numbers in brackets give the relative reactivities of the compounds referred to the slowest as unity. The relative velocities depend to some extent on the concentrations for which the measurements are made—the above values are valid for $N/30$ solutions of the reacting substances.

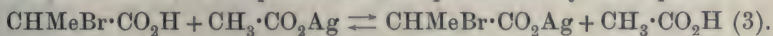
The velocities of these reactions have already been compared with those in which the halogen has been displaced in the presence of water alone, and when the sodium salts are acted on by alkali, and it has been pointed out that the reactions in which silver salts are employed are much more rapid. The reactions now under consideration also differ from those described in the previous papers as regards the magnitude of the difference in the reactivities. It is not usually considered that the substitution of a methyl group

for hydrogen makes a very serious difference in the reactivity of adjacent groups, and yet bromopropionic acid is a hundred times more active than bromoacetic acid as regards silver nitrate. It is hoped that measurements with the corresponding esters will throw some light on the causes of this remarkable difference.

The fact that the sodium salts of the bromo-fatty acids react more rapidly than the free acids with silver nitrate is doubtless connected with the fact that the concentration of silver salt is higher in the former solutions than in the latter. The equilibria in the case of bromopropionic acid are represented by the equations:



As bromopropionic acid is a relatively weak acid, the equilibrium for reaction (1) will be displaced towards the right to a smaller extent than in equation (2), and therefore the concentration of silver bromopropionate—perhaps the substance which really reacts—will be smaller in the former case than in the latter. Similar considerations account for the fact that the initial rate of reaction of silver acetate is greater than that of silver nitrate (p. 355). In the former case, the equilibrium is represented by the equation:



and owing to the fact that acetic acid is a much weaker acid than bromopropionic acid, the equilibrium will be displaced towards the right, and the concentration of silver bromopropionate will be relatively great.

Another way of interpreting these results is to assume that it is the $\text{CHMeBr} \cdot \text{COO}'$ ion which reacts with silver nitrate. It can easily be calculated that the ratio of the $\text{CHMeBr} \cdot \text{COO}'$ ion concentration in sodium bromopropionate and bromopropionic acid in *N*/30 solution is about 4·5 : 1, which approximates to the ratio of their reactivities with silver nitrate. Similarly, the $\text{CH}_2\text{Br} \cdot \text{COO}'$ ion concentration in sodium bromoacetate and the free acid is about 4 : 1, whilst the ratio of their reactivities with silver nitrate is about 3 : 1.

The suggestion that it is mainly the ions of the bromo-fatty acids which react with silver nitrate is further supported by the experiments with nitric acid (p. 351). It can readily be calculated that the $\text{CHMeBr} \cdot \text{COO}'$ ion concentration in *N*/20-bromopropionic acid is reduced to about 1/7th of its value by the addition of *N*/15-nitric acid, which is just the ratio in which the reactivity of bromopropionic acid towards silver nitrate is reduced by the same proportion of nitric acid.

The fact that the rate of reaction is approximately proportional

to the concentration of the bromopropionic acid instead of to the square root of the concentration (p. 348) appears at first sight to be opposed to the view that the ions are the active agents, but this may be due to complications arising from the catalytic influence of the silver bromide.

There is no conclusive evidence as to what function of the silver nitrate is concerned in these reactions, but the fact that sodium nitrate retards the reaction considerably speaks rather for the view that the Ag^+ ions are the main active components. Should this suggestion prove, on further investigation, to be well founded, an interesting explanation of the great reactivity of bromo-fatty acids with silver salts may be given on the basis of considerations developed in a previous paper (compare Trans., 1909, **95**, 1839). It has been suggested that the relatively slow reaction between $\text{CH}_3\cdot\text{CHBr}\cdot\text{COO}'$ ions and OH' ions is connected with the mutual repulsion of the negative charges, and it may therefore be anticipated that the reaction between the $\text{CH}_3\cdot\text{CHBr}\cdot\text{COO}'$ ion and a positively charged ion (in this case the Ag^+ ion) will be relatively rapid (compare table, *loc. cit.*, p. 1835).

The interpretation of the results is complicated by the equilibria represented by equations (1), (2), and (3) (p. 361). An attempt will be made to prepare pure silver bromopropionate and measure its reactivity, but owing to the great instability of the salt it will probably be difficult to obtain trustworthy results.

In conclusion, I desire to thank Mr. R. W. Davies and Mr. T. J. Ward, of St. Mary's Hospital Medical School, for valuable assistance in the experimental part of the work.

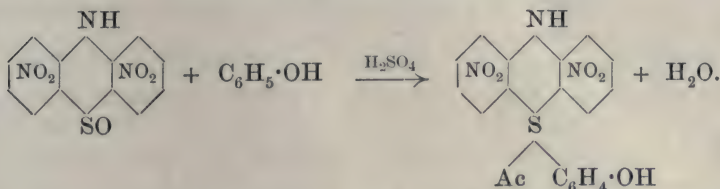
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XL.—*Derivatives of S-Phenylphenazothionium.* *Part III.*

By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

In two previous communications (Hilditch and Smiles, Trans., 1908, **93**, 145, 1687) the products obtained by the condensation of the nitrodiphenylamine sulphoxides with phenol and phenetole were described. Reasons were then adduced for regarding these sub-

stances as derivatives of *S*-phenylphenazothionium, the process by which they are formed being formulated as follows:

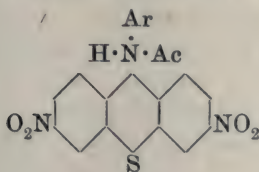


In the meantime the study of the intramolecular rearrangement of the diphenylamine *o*-sulphoxides (Trans., 1909, **95**, 1253; this vol., p. 186) has enabled us to obtain evidence throwing further light on the formation and reactions of these substances. We have therefore extended our experiments with derivatives of this group in order further to discuss their constitution and chemical behaviour.

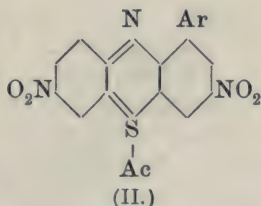
In the first part of this paper the constitution of these derivatives is discussed, and in the latter part the factors governing their formation are considered.

I.—The Constitution of the Derivatives.

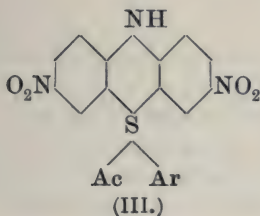
When dinitrodiphenylamine *o*-sulphoxide is treated with a phenol or its ether in presence of concentrated sulphuric acid, the sulphates of the dinitro-compounds of the group are formed. In discussing the constitution of these substances, it has been pointed out (Trans., 1908, **93**, 1688) that on general grounds only three alternative structures can be entertained; these respectively involve the *N*-aryl (I), the *C*-aryl (II), and the *S*-aryl (III) arrangements:



(I.)



(II.)



(III.)

Ample reasons have been already given for discarding the former alternatives (I and II) and for accepting the *S*-aryl structure as the true representation of these salts. Later experiments have served still further to strengthen this conclusion.

The N-Aryl Structure.—In order further to test the validity of this structure, we have prepared *N*-phenylthiodiphenylamine by means of the reaction devised by I. Goldberg (*Ber.*, 1907, **40**, 4525) for the phenylation of aromatic amines, and we find that the properties of this substance and its nitro-derivatives are entirely different from those of the compounds the structure of which is in question.

N-Phenylthiodiphenylamine.

A mixture of 10 grams of iodobenzene, 5 grams of thiodiphenylamine, 4 grams of potassium carbonate, and 0.5 gram of copper iodide was boiled with excess of bromobenzene for eighteen hours in a flask provided with a reflux arrangement. Water was then added, and the volatile benzene derivatives were removed with the aid of a current of steam. The solid residue was boiled with alcohol, and the solution was separated from the residue by filtration. The product remaining in the filtrates usually contains a considerable quantity of unchanged thiodiphenylamine, but by crystallisation of the more soluble portion, *N*-phenylthiodiphenylamine was obtained in short, yellow prisms, which melted at 89—90°:

0.2006 gave 0.5790 CO₂ and 0.0906 H₂O. C=78.7; H=5.0.

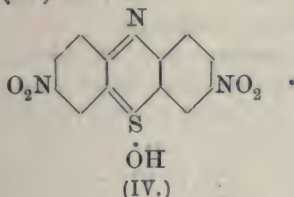
C₁₈H₁₃NS requires C=78.5; H=4.7 per cent.

In chemical behaviour the substance closely resembles *N*-methylthiodiphenylamine. It is soluble in concentrated sulphuric acid, giving a crimson solution, being then partly oxidised to the phenazothionium salt. The basic properties, if, indeed, any are manifest, are very weak, since no salts could be isolated. When nitrated under the conditions required to obtain the dinitro-sulphoxide from *N*-methylthiodiphenylamine, the substance furnishes a mixture of polynitro-compounds, which could not be satisfactorily separated. However, it is sufficient for the present purpose to record the properties of the nitrated substance. It is crystalline, yellow in colour, insoluble in and unattacked by aqueous alkali hydroxide, and, like the corresponding *N*-methyl derivative, may be condensed with phenetole in presence of concentrated sulphuric acid. It is very soluble in cold glacial acetic acid. The following table is given in order to emphasise the distinction between these derivatives and the condensation product obtained from dinitrodiphenylamine *o*-sulphoxide and phenetole:

	<i>N</i> -Phenylthio- diphenylamine.	Nitro- derivatives.	Condensation product from phenetole and dinitro- diphenylamine sulphoxide.
Colour of base	Yellow	Yellow	Crimson and fluorescent in solution.
Action of acids on base.	No salts formed		Stable green salts ob- tained.
Action of H ₂ SO ₄ and phenetole.	—	Condensation	Salt formed, but no further action.

The fact that *N*-phenylthiodiphenylamine and its nitro-derivatives do not form salts, whilst the green salts in question are quite stable, is alone sufficient to show that the latter do not contain the *N*-aryl structure. Moreover, if these salts contain the *N*-aryl structure (I), it is clear that the action of alkali must furnish a dinitro-*N*-phenylthiodiphenylamine, but instead they yield crimson, fluorescent bases (Trans., 1908, **93**, 151, 1693), which are entirely different from the nitro-derivatives of *N*-phenylthiodiphenylamine. For these reasons the *N*-aryl structure for these compounds must be finally rejected.

The C-Aryl Structure (II).—It was previously shown (Trans., 1908, **93**, 1689) that if this structure were correct, the substance must be formed by simultaneous oxidation of the phenol and the phenazothionium salt (IV):

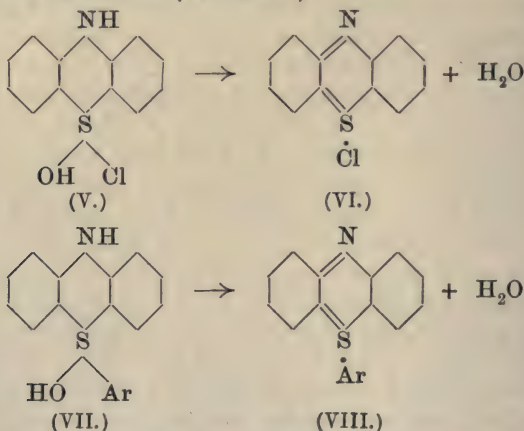


According to this view, the latter substance would appear as an intermediate product formed from the dinitro-sulphoxide (I) by the action of the concentrated acid (see Trans., 1909, **95**, 1261). Much evidence has already been adduced for abandoning this view, but, since it is now possible to obtain the dinitrophenazothionium hydroxide in the pure condition, we have been able to submit the question to direct test. Numerous attempts were made to effect the condensation of this phenazothionium hydroxide with phenetole by means of concentrated sulphuric acid both without and in presence of a mild oxidising agent, but they were unsuccessful. In these experiments the greater portion of the phenazothionium hydroxide was unattacked, whilst the remainder was converted into a tarry material from which no definite product could be isolated. However, more cogent argument against this structure is furnished by a comparison of the properties of the dinitrophenazothionium hydroxide and the phenolic compound the constitution of which is sought. It has been elsewhere shown (Trans., 1909, **95**, 1256) that

in the former substance (IV) the basic function of the azothionium group is depressed by the presence of the nitro-groups in the adjacent benzene nuclei; in fact, the substance does not form salts with aqueous mineral acids. But on examining the formula (II) which represents the *C*-aryl structure for the phenolic compound, it will be seen that, if this were correct, the substance must exhibit a similar lack of basic properties, for it cannot be supposed that these would be strengthened by the linking of a phenolic residue to one of the aromatic nuclei in the azothionium complex. Since all the dinitro-compounds of this group which have been obtained exhibit well-defined basic properties, it is clear that they cannot be derived from the *C*-aryl structure, which for this and other reasons (*Trans.*, 1908, **93**, 1689) must now be finally rejected.

The S-Aryl Structure.—This constitution now remains as the only possible alternative, and, as previously shown (*Trans.*, 1908, **93**, 1687), it is to be anticipated from the characteristic behaviour of the thionyl group in aromatic sulfoxides, since the latter substances are converted into sulphonium salts by treatment with aromatic compounds in presence of phosphoryl chloride or sulphuric acid. It will now be shown that the *S*-aryl structure is further justified by the analogy between these substances and the parent phenazothionium compounds.

In discussing the mechanism of the change of the imino-thionyl structure into the azothionium arrangement, it has been demonstrated (this vol., p. 186) that in this reaction the thionyl salts are first formed, and that these are subsequently converted into the quinonoid compounds. The process, reduced to its simplest terms, is represented as follows (V and VI):

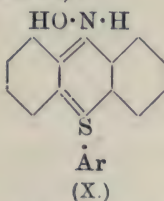
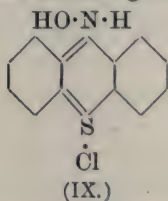


Now, when the *S*-aryl salts are treated with aqueous alkali hydroxide, they are converted by loss of the elements of mineral

acid into crimson, fluorescent bases (Trans., 1908, **93**, 145), for which the quinonoid structure (VIII) is accordingly the only representation possible. It is clear that in this process the sulphonium hydroxides (VII) must be first produced by the action of the alkaline reagent, and on referring to the formulæ it will be seen that the conversion of these substances into the quinonoid base is strictly analogous to the change of sulphoxide salt into the quinonoid sulphonium salt (V and VI). In either case the quinonoid arrangement is produced by removal of hydroxyl from the quadrivalent sulphur group.

In both series it is possible to obtain the quinonoid derivatives in the hydrated condition. If the green *S*-aryl salts are boiled with water or treated with cold aqueous sodium carbonate, the crimson hydrated bases are formed (Trans., 1908, **93**, 151, 1693).

In a previous paper dealing with the salts and hydrates of phenazothionium (this vol., p. 186), we have shown that there is good reason for representing this additional molecule of water as forming the ammonium grouping (as in IX):



If this hypothesis is extended to the *S*-phenyl derivatives, the formula (X) forecasts the possibility of the existence of two series of salts: the green or yellow sulphonium salts (type III), as obtained with the dinitro-derivatives, and a red series, which would be the ammonium salts (type X). We have been able to show that the latter exist. The sulphonium grouping in the dinitro-derivatives which give the green salts is of moderate basic power, and it is evident that if these red ammonium salts exist they must be sought for in derivatives where the basic properties of the sulphonium group are still further depressed. With this object in view the tetranitro-derivative of this series was investigated.

Tetranitro-S-phenetylphenazothionium.

Finely powdered tetranitrodiphenylamine *o*-sulphoxide was mixed with a large excess of concentrated sulphuric acid. Some of the sulphoxide dissolved, but the greater portion remained in suspension. Excess of phenetole was then gradually added to the cold mixture, which was constantly agitated and kept within the limits of atmospheric temperature. As increasing quantities of the

phenolic ether were added, the suspended sulfoxide dissolved, forming a deep red solution. When renewed addition of the reagent produced no further change, the mixture was passed through glass wool, and then poured on a large bulk of melting ice. The now insoluble reddish-brown material was collected, well washed with cold water, and finally dried at the atmospheric temperature. This crude material was purified by rapid extraction with acetone in a Soxhlet apparatus. The acetone solution resulting from this operation was concentrated on the water-bath, and then, when cold, it was mixed with a little ether. The first precipitate was removed by filtration and rejected; but on adding a further quantity of ether to the filtrates, *tetranitro-S-phenetylphenazothionium sulphate* was gradually precipitated in minute, reddish-brown crystals. Analysis was conducted with two samples from different preparations:

0.1877 gave 0.2728 CO_2 and 0.0553 H_2O . $\text{C}=39.65$; $\text{H}=3.2$.

0.1328 „ 0.1937 CO_2 „ 0.0391 H_2O . $\text{C}=39.8$; $\text{H}=3.2$.

$\text{C}_{20}\text{H}_{13}\text{O}_9\text{N}_5\text{S}, \text{H}_2\text{SO}_4$ requires $\text{C}=40.2$; $\text{H}=2.5$ per cent.

The substance does not melt below 250° ; it is insoluble in water or cold alcohol, and soluble in acetone. The solutions in the last-named solvent are not fluorescent, like those of the dinitro-compounds.

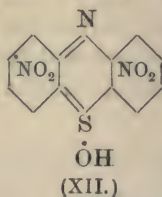
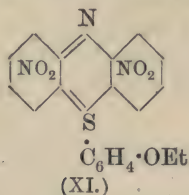
The *base* is readily obtained in the hydrated form by boiling the sulphate with water. A sample, which had been dried in the steam-oven, was analysed:

0.2014 gave 0.3404 CO_2 and 0.0652 H_2O . $\text{C}=46.1$; $\text{H}=3.6$.

$\text{C}_{20}\text{H}_{13}\text{O}_9\text{N}_5\text{S}, \text{H}_2\text{O}$ requires $\text{C}=46.4$; $\text{H}=2.9$ per cent.

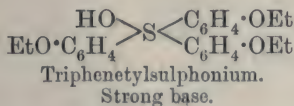
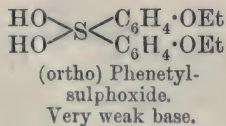
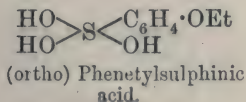
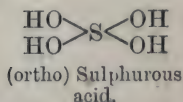
Tetranitro-S-phenetylphenazothionium hydroxide is insoluble in water, and very sparingly soluble in boiling alcohol.

Finally, on comparing the dinitro-compounds of the *S*-phenyl series (XI) with those of the parent series (XII):



it is seen that in the former class the basic function of the sulphonium group is appreciably increased by the substitution of aryl for hydroxyl at the quadrivalent sulphur. But it may be remarked that this increase in basic power is to be expected from the general influence of this substitution in simpler compounds of

quadrivalent sulphur. The following series is quoted to illustrate this effect:



and it is clear that the successive replacement of the hydroxyl groups in ortho-sulphurous acid gradually increases the basic power of the group in question.

From these considerations it is seen that the chemical behaviour of the condensation products agrees very closely with that which would be expected for them on the basis of the *S*-aryl structure from analogy to the simpler phenazothionium hydroxides. Moreover, since all other possible structures have been shown to be untenable, the *S*-aryl constitution must now be regarded as finally established.

II.—Formation of the *S*-Arylphenazothionium Arrangement.

The factors which control the formation of these derivatives are to be found in the nature of the diphenylamine *o*-sulphoxide employed and in the group which is to enter the thionium arrangement. These will be considered separately.

(a) *The Influence of the Character of the Sulphoxide*.—It has been previously mentioned that the derivatives of the *S*-aryl series are obtained by the condensation of a diphenylamine *o*-sulphoxide with an aromatic compound in presence of concentrated sulphuric acid (see formulæ on p. 363). But by no means do all the sulphoxides of diphenylamine behave in this manner. Previous experiments (Trans., 1909, **95**, 1253) have shown that, when treated with acid reagents, some of these sulphoxides are immediately converted into salts of phenazothionium (V and VI), and the latter substances are incapable of undergoing the required condensation. It is therefore evident that the answer to the question whether a given sulphoxide can yield the *S*-aryl derivatives by this reaction must depend on the stability of the sulphoxide in presence of the strong acid. If the sulphoxide is instantaneously converted by the acid into the phenazothionium salt, the *S*-aryl derivative will not be formed; but if this conversion does not take place, or if it is sufficiently slow to enable the condensation to be effected before it has proceeded far, then the *S*-aryl derivatives

can be obtained. This is entirely borne out by the behaviour of the six sulfoxides which have been examined:

Sulphoxide.		In concentrated H_2SO_4 .	In concentrated H_2SO_4 with phenetole.
Diphenylamine	<i>o</i> -sulphoxide	Immediate rearrangement	No condensation.
<i>N</i> -Methyldiphenylamine	"	"	"
<i>pp</i> -Dinitrodiphenylamine	"	Rearrangement slow	"Condensation with fresh solutions.
Diisnitrodiphenylamine	"	"	Condensation with fresh solutions.
Dinitro- <i>N</i> -methyldiphenylamine <i>o</i> -sulphoxide.		"	Condensation with fresh solutions.
Tetranitrodiphenylamine	<i>o</i> -sulph- oxide.	No rearrangement ap- preciable.	Condensation.

Of these six cases, those of the dinitro-derivatives are the more noteworthy. When phenol is added to freshly prepared solutions of these substances, the *S*-hydroxyphenyl derivatives are readily formed, and the yield is almost quantitative; but with solutions which have been kept some hours, the required reaction does not take place. The intramolecular rearrangement of these sulfoxides which thus militates against the formation of the *S*-aryl derivatives is favoured by the increase of the basic function of the thiodiphenylamine nucleus (this vol., p. 186). Hence it is clear that the introduction of basic groups in the sulfoxide will tend to hinder the formation of the *S*-aryl compounds, and the addition of acidic groups will tend to exert a favourable influence. This favourable effect seems to attain a maximum in the dinitro-compounds, for these are more reactive and furnish better yields than the tetranitro-derivative. It appears that in these substances the thionyl group is still sufficiently basic to yield readily the sulfoxide salts (V) which form the preliminary stage of the reaction (Smiles and Le Rossignol, *Trans.*, 1906, **89**, 697). The more sluggish condensation of the tetranitro-derivative may be ascribed to the lessened tendency to form these salts, which is due to the further addition of acidic substituents.

(b) *The Nature of the Groups which may enter the Thionium Arrangement.*—Experiments have shown that the chief types of simple aliphatic compounds do not furnish these sulphonium derivatives under the normal conditions of the reaction. The formation of these derivatives seems confined to compounds containing an aromatic complex or an arrangement similar thereto.

The capability of an aromatic compound to condense with the diphenylamine sulfoxide is determined by the reactivity of the aromatic nucleus in the compound in question, and this, in turn, depends on the number and nature of the substituents present.

Of the aromatic hydrocarbons, benzene and toluene are inactive, but if suitable groups are introduced, the condensation can be

readily effected, for example, *m*-xylene acts very sluggishly, but from mesitylene the sulphonium base is easily obtained.

Dinitro-S-mesitylphenazothionium.

Excess of mesitylene was slowly added with constant agitation to a freshly prepared ice-cold solution of *pp*-dinitrodiphenylamine sulphoxide in concentrated sulphuric acid. After each addition of the hydrocarbon, a sample of the liquid was withdrawn and poured into cold water. When the precipitate obtained in this manner was of a pure green colour, the addition of the hydrocarbon was interrupted, and the reaction mixture was poured on powdered ice. The sulphate was then collected and washed, first with water and then with ether, to remove adherent mesitylene and other oily impurities. After renewed washing with water, the salt was triturated with a cold aqueous solution of sodium carbonate. The solid base was collected, and washed with water until free from alkali. After purification, *dinitro-S-mesitylphenazothionium hydroxide* was obtained in minute, chocolate-brown crystals of high melting point. A sample which had been dried at 100° was analysed:

0.2024 gave 0.6660 CO₂ and 0.0868 H₂O. C=59.8; H=4.7.

C₂₁H₁₇O₄N₃S.H₂O requires C=59.3; H=4.47 per cent.

The base is sparingly soluble in hot water, giving purple solutions, and readily so in cold acetone.

Generally speaking, however, the reactivity of the hydrocarbons is sluggish in comparison with the hydroxy- and amino-derivatives of benzene. Qualitative experiments made with a wide range of material have shown that almost all aromatic compounds containing these groups alone readily furnish the *S*-aryl derivatives with the dinitro-sulphoxides. But since the products obtained from these substances for the greater part resemble the *S*-hydroxy-phenyl and -phenetyl derivatives which have already been described in detail, no particular interest would have been served by the isolation and analysis of each compound. However, the case of the *S*-salicyl derivative is worth especial mention, since it occurs as a true carboxy-thetine.

Dinitro-S-salicylphenazothionium.

The condensation of *pp*-dinitrodiphenylamine sulphoxide with salicylic acid was effected in the usual manner. The crude product, after being well washed with cold water, was dissolved in dilute aqueous alkali hydroxide. The solution was then clarified by filtration, and then mixed with dilute sulphuric acid in exactly

sufficient quantity to precipitate the thetine. No suitable solvent could be found for the recrystallisation of this substance. It is soluble in hot nitrobenzene, but on cooling the solution it is precipitated in the amorphous condition. Analysis was made with a sample which had been washed with alcohol and dried in the steam-oven:

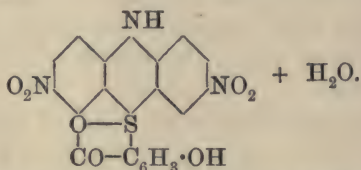
0.2036 gave 0.3858 CO_2 and 0.0608 H_2O . $\text{C}=51.6$; $\text{H}=3.2$.

0.1510 „ 12.5 c.c. N_2 at 23° and 750 mm. $\text{N}=9.4$.

$\text{C}_{19}\text{H}_{13}\text{O}_8\text{N}_3\text{S}$ requires $\text{C}=51.6$; $\text{H}=2.9$; $\text{N}=9.7$ per cent.

Dinitro-S-salicylphenazothionium hydroxide forms a mustard-yellow, amorphous powder of high melting point.

It is worth observing that the substance obtained in this manner is not the sulphate of the *S*-aryl base which might be expected from analogy to the *S*-hydroxyphenyl derivative. Evidently the sulphonium salt is internally formed with the carboxyl group, the additional molecule of water being present as with most thetines and betaines:



The substance is more stable than the salts of the *S*-hydroxyphenyl series, being unattacked by boiling water; but it is soluble in alkali, giving deep red solutions of a sodium salt.

Turning to the condensation products obtained from naphthalene derivatives, it has been found that the wide scope of the reaction observed with benzenoid compounds is well sustained. Although naphthalene itself does not react with the dinitro-sulphoxides, all hydroxy- and amino-derivatives which have been examined readily form the *S*-naphthyl derivatives. These possess well-defined tinctorial properties, and when sulphonic groups are present the compound is readily soluble in cold water; but the simple hydroxy- and amino-derivatives are sparingly soluble. Some of the chief examples of the *S*-naphthyl derivatives are described in the following table:

Condensation of the <i>pp</i> -Dinitro-sulphoxide with	Colour.
α -Naphthylamine	Purple; sparingly soluble.
β -Naphthylamine	Reddish-brown; sparingly soluble.
α -Naphthol	Blue; sparingly soluble.
2-Naphthylamine-6:8-disulphonic acid ..	Crimson; soluble.
2-Naphthylamine-6-sulphonic acid	Crimson; „
2-Naphthol-6:8-disulphonic „	Brown; „ violet in alkali.
2-Naphthol-3:6-disulphonic „	Crimson; „
2-Naphthol-6-sulphonic „	Olive green, violet in alkali.

Attempts to purify and to obtain these derivatives in the crystalline state have been unsuccessful, since they persistently remain in the colloidal condition. The physical properties of the α -naphthol derivative are perhaps worth special mention. After undergoing a process of purification, this substance was finally obtained as a blue, viscous jelly, which, on being broken by shock, exhibited a dry fracture.

These *S*-aryl derivatives of phenazothionium are not formed by all aromatic compounds, the most prominent exceptions being the simple nitro-derivatives of benzene and naphthalene. From a general point of view the reaction may be said to be controlled by conditions similar to those observed in the process of sulphination (Trans., 1908, **93**, 745), but hitherto the influence of the so-called steric conditions has not been observed. The resemblance between these processes is not surprising, since the formation of the *S*-aryl phenazothionium salts from the sulfoxides is evidently analogous to the third stage in the ordinary process of sulphination where the triaryl-sulphonium salt is formed from the sulfoxide.

Finally, it is necessary to point out that the condensation of the thionyl group in the dinitro-sulphoxide is not confined solely to aromatic compounds. For example, thiophen readily furnishes the *S*-thienyl derivative.

S-Thienylphenazothionium.

The condensation of thiophen with *pp*-dinitrodiphenylamine sulfoxide was effected in the usual manner; but since much charring takes place during the reaction, the reagents were employed only in small quantity at each operation, and the temperature was kept below 5°. The impure sulphate, obtained by pouring the united reaction mixtures into water, was collected, washed first with water, and then with alcohol, and finally triturated with aqueous sodium carbonate. The impure base was collected, washed, and dried in the steam-oven. The dry product was crushed to a fine powder, and rapidly extracted with a little acetone to remove soluble impurities. The remaining product was crystallised from boiling phenetole, which, on cooling, deposited *dinitro-S-thienylphenazothionium hydroxide* in large, red prisms, which exhibited a steel-blue lustre. The substance is very sparingly soluble in cold acetone, and does not melt below 250°:

0.2032 gave 0.3828 CO₂ and 0.0330 H₂O. C=50.6; H=1.8.

C₁₆H₉O₄N₃S₂·½H₂O requires C=50.5; H=2.6 per cent.

From the analytical data it appears that the normal sulphonium hydroxide has lost water during the recrystallisation from the high

boiling solvent; unfortunately the quantity of material was too small to enable the analysis to be repeated.

In conclusion, we desire to express our thanks to Dr. Cain for kindly lending us samples of the various amino- and hydroxy-sulphonic acids of naphthalene which were employed in this investigation. We also wish to thank the Research Fund Committee of the Society for a grant which has defrayed the expense of this research.

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XLI.—*Apparatus for Demonstrating the Electrolysis of Hydrochloric Acid.*

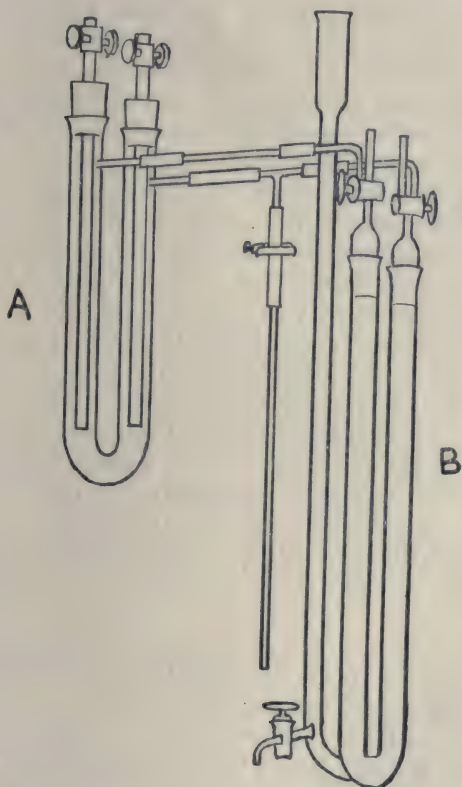
By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

THOSE who have occasion to use Hofmann's apparatus for showing the electrolytic decomposition of hydrochloric acid into equal volumes of its constituent gases, soon become aware that its comparative simplicity has been attained only at the cost of some disadvantages. Of these it is sufficient to mention (i) the leakage of the acid electrolyte at the bottom of the H-shaped tube; (ii) a difficulty in ascertaining when the saturation with chlorine is complete; and (iii) the possibility, in certain circumstances, of the two gases becoming mixed. Various devices have been proposed to obviate these troubles; they are, however, not very satisfactory in practice, and in any case, when it comes to the final demonstration, there is always distinct inequality between the volumes of the liberated gases.

In L. Meyer's improved apparatus (*Ber.*, 1894, **27**, 850), the simplicity is abandoned; for, whilst Hofmann's original form of voltameter is retained, the gases are delivered apart, under diminished pressure, into separate tubes, one of which, containing water, serves to collect the hydrogen; the other, filled at first with saturated chlorine-water, receives the chlorine; each of these tubes, open below, stands in a trough of the liquid with which it is charged. Over the earlier form Meyer's modification has one distinct advantage, since by means of it the equality in volume of the resultant gases may be demonstrated; on the other hand, not only must saturated chlorine-water be prepared, and the collecting

tube filled with it, but also the exposure, on the lecture-table, of an open dish charged with this liquid is not free from objection. Moreover, the three disadvantageous features mentioned above are not eliminated.

The apparatus here figured, although less simple than that of Hofmann, is sufficiently compact to be set up on a single stand, and in practice has given results that are satisfactory. Briefly, it consists of two parts: A, the electrolyser, and B, the vessel for



receiving and measuring over concentrated sulphuric acid the gases delivered from A.

The electrolyser is a U-tube of 1-inch bore, having near each end a delivery tube, as shown; a well-paraffined cork in each neck carries a half-inch carbon cylinder, one foot long; to the projecting free end of this rod a brass binding screw is clamped.

The collecting and measuring vessel is a tall U-tube, of some five-eighths to three-quarters of an inch in bore and about 14

inches long, to the lowest point of which another tube (the pressure-tube) is sealed as shown, to end in a bulb above the highest point of the U; at the foot of the pressure-tube, just where it begins to bend upward, is sealed on a light glass tap, having its axis parallel to the plane of the U-tube. Into the top of each measuring tube is ground a hollow glass stopper, which terminates in an obliquely bored two-way tap, communicating at will, either with a short stand-tube of about one-eighth of an inch in bore and an inch or so in length, or with the bent receiving tube, just alongside; the distance between the latter and its fellow of the opposite side is such that each is in a straight line with the corresponding delivery tube of the electrolyser.

By suitable pieces of glass and rubber tubing, the two main parts are connected as shown, the hydrogen-connexions being made with butt-joints and thick-walled rubber tube, well smeared inside with glycerol; between the chlorine delivery tube and the corresponding receiving tube a T-piece may conveniently be introduced; this, when provided with rubber connexion, pinchcock, and glass delivery tube, serves to pass the waste chlorine, when desired, to the table-draught, or into a beaker of lime.

When the electrolyser is filled, the electrolyte may reach to within an inch of the delivery tubes. The receiver is charged in all three limbs to the level of the bottoms of the stoppers, where ground in to the measuring tubes; the sulphuric acid used for filling may be stained, if the operator wishes, by a method given below. The parts are now connected; the pinchcock is opened, both gas-taps are turned into position for receiving, and the plug of the one for hydrogen pulled out sufficiently to allow this gas, when liberated, to pass freely out from the electrolyser into the air.

The current is now turned on, and maintained until the chlorine is seen to be escaping freely. To ascertain if saturation is complete, the pinchcock is closed, the chlorine-tap pulled out for a moment from its seat to equalise pressure, then both taps are pushed home simultaneously, and the lowest tap is turned on, so that the gases may accumulate in the collecting tubes under a pressure not greater than the atmospheric, or less, as may be desired. There is no difficulty in knowing if saturation is complete, for, when this stage is attained, the two tubes fill at exactly the same rate from start to finish.

To recharge the collecting vessel, the pinchcock is opened, the plug of the hydrogen-tap pulled out as at first, and the sulphuric acid, which was drawn off, is returned to the apparatus through the bulb at the top; after this the procedure is as before. When

the production of the two gases in equal volumes has been demonstrated, the acid may be returned to the bulb, and the gases, displaced through the two short stand-tubes, may be proved, in the usual way, to be hydrogen and chlorine respectively.

It is scarcely necessary to mention that the slowness (one can hardly call it speed) of saturation with chlorine varies considerably, according to whether the electrolyte is hydrochloric acid alone, the same saturated with salt, or saturated brine; in every case the tediousness is, of course, much reduced by preliminary saturation of the electrolyte with chlorine.

In conclusion, a few points may be noted. The gas-taps should be smeared with vaseline as lightly as will suffice to render them gas-tight; otherwise more or less chokage may occur; the butt-joints, etc., are recommended for the hydrogen connecting tubes on account of the facility with which this gas escapes through rubber; and the cork joints, of course, must be made tight with paraffin or other suitable luting; also, the carbon rods, when done with, should be well washed and dried, to prevent disintegration. It is not easy for persons sitting at a distance to see clearly the accumulation in a narrow tube of colourless or faintly-coloured gases over a colourless liquid. With the apparatus here described, this difficulty may be overcome by dissolving in the sulphuric acid enough chrome-alum to stain it deep green; if between the collecting tubes and the pressure-tube a sheet of milk-glass be interposed, with a light close behind, the filling of the former is rendered easily visible from any part of an ordinary lecture-room. The glass parts of this apparatus were made by Messrs. Baird and Tatlock, in accordance with drawings supplied to them.

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CORK.

XLII.—*The Solubility of Potassium Sulphate in Concentrated Aqueous Solutions of Non-Electrolytes.*

By JOHN JACOB FOX and ARTHUR JOSIAH HOFFMEISTER GAUGE.

IN a recent communication (Trans., 1909, **95**, 885) one of us showed that the solubility of potassium sulphate in water at 25° was decreased markedly by the presence of potassium acetate. Since the rate of the decrease is much greater with the more dilute solutions of potassium acetate, which are dissociated electrolytically to a greater degree than the stronger solutions, the

presence of the potassion due to ionised potassium acetate might be considered as being the main factor in decreasing the solubility of potassium sulphate as distinct from the general effect of the second substance in solution, in this case non-ionised potassium acetate. With the view of gaining some further knowledge as to the action as precipitant of the second substance in solution, it was thought desirable to determine the effect on the solubility of potassium sulphate of a number of non-electrolytes, and to ascertain whether the nature of the non-electrolyte was to any marked degree concerned in the action. In the case of potassium sulphate a few determinations of this character have already been carried out, and the general result, both with electrolytes and non-electrolytes, is that the solubility of potassium sulphate in aqueous solution is depressed. From the point of view of the present communication the results of most interest are those of Girard (*Bull. Soc. chim.*, 1885, [ii], **43**, 552) for the solubility of potassium sulphate in aqueous ammonia, and of Rothmund and Wilsmore (*Zeitsch. physikal. Chem.*, 1902, **40**, 619) for the solubility in aqueous acetic acid and aqueous phenol.

While these results are similar to those described below, a strict comparison cannot be made, since the alteration of solubility by volume has been used by these observers, whereas we prefer the alteration in solubility referred to a fixed quantity of water. A fair approximation to the depression of solubility by volume can, however, be deduced if it is assumed that the total of the volumes of the potassium sulphate and of the liquid in which it is dissolved does not alter. This gives a volume too great by rather more than 1 per cent. in the stronger solutions of potassium sulphate, and practically correct in the weaker solutions. Thus it was found that aqueous alcohol, D_{25}^{25} 0.9913, yielded a solution containing 7 per cent. of potassium sulphate, and having a density of 1.0499. The density of finely powdered potassium sulphate was found to be 2.656 at 20°/20°. Hence 100 c.c. of the saturated solution should, from the composition, occupy 101.3 c.c. Similarly, a solution of glycerol and water, containing 7.2 per cent. of potassium sulphate, possessed a density of 1.1029, the original glycerol and water having a density of 1.0420. The calculated volume of 100 c.c. is 101.2 c.c. As most of the solutions contain less than 7 per cent. of potassium sulphate, the errors introduced are less. Using these calculated volumes, it will be found that the nature of the curves obtained is similar to that of Rothmund and Wilsmore referred to above.

The substances used by us were ethyl alcohol, ethylene glycol, glycerol, mannitol, chloral hydrate, sucrose, acetone, and pyridine.

The solutions were examined partly from the point of view of the possible formation of definite hydrates, since it was thought possible that if with any mixture a simple hydrate was formed, a change in the solubility curve at this point would be found. With this object, mixtures with water in all proportions were taken, and the solubilities plotted against the percentage composition of the aqueous solution.

This method of plotting was chosen in preference to the method of reference to a fixed quantity of water, because of the difficulty of deciding whether water should be considered as solvent or solute in concentrated solutions.*

It is obvious from the curves that as the number of hydroxyl groups in the molecule increases, the precipitating effect of the non-electrolyte decreases, and if the curves are drawn with molecules of potassium sulphate as ordinate and non-electrolyte as abscissæ, taking 1000 molecules of water as fixed, the result is the same. Whether this would be found to apply to other salts cannot, of course, be decided without further investigation. None of the curves give any indication of discontinuity, so that on this view the existence of definite simple hydrates is negatived. This does not, of course, imply that the substances dissolved do not form complexes with more or less water, but the most the results set forth here can be said to indicate is that the non-electrolyte and water exert a material influence on each other, the action preventing the water from dissolving the full amount of salt. There is one consideration, however, which is in a measure opposed to the results obtained by Jones and Getman from observations of the depression of the freezing point of aqueous solutions of non-electrolytes (*Amer. Chem. J.*, 1904, **32**, 308). From these observations, Jones and Getman conclude that the deviations of the observed values of the freezing point from the theoretical value are due to the formation of complexes of the solute and water; that in so far as some of the water is used up to form hydrates, less water remains to function as solvent for the hydrate, and that therefore abnormally high results for depression of freezing point are obtained. It should follow that if some of the water is prevented from acting as solvent in the case of hydrates, the same effect should be shown when a second substance (for example,

* During the course of this work, a paper by Rothmund appeared (*Zeitsch. physikal. Chem.*, 1909, **69**, 523), dealing with a somewhat similar problem, but using comparatively dilute solutions of the various alcohols and other organic substances. Their effects as precipitants were studied in the case of lithium carbonate and other sparingly soluble salts. Rothmund used fixed volume, and this is justified since the volume of the original solutions could be altered but slightly by the dissolution of sparingly soluble salts.

potassium sulphate) is dissolved in the solution. Philip has demonstrated this to be the case when hydrogen is dissolved in aqueous sucrose solutions (Trans., 1907, **91**, 711). Now, according to Jones and Getman, alcohol, chloral hydrate, and mannitol do not show any marked tendency to form hydrates, whereas sucrose, and particularly glycerol, show considerable hydration. We should therefore expect alcohol, chloral hydrate, and mannitol to exert less influence on the solubility of potassium sulphate than either glycerol or sucrose. As will be seen from the results here given, the reverse is the case, both alcohol and chloral hydrate being much more marked in their action than glycerol or sucrose, whether the curves are drawn up on the percentage basis as in the figure, or on the basis of a fixed 1000 molecules of water. It may be argued that the results are in part explicable on the assumption that unless ions are hydrated they cannot exist in aqueous solutions, and consequently that the potassium sulphate will not dissolve if the ions derived from it are subjected to conditions which tend to dehydrate them. The presence in solution of hydrated non-electrolytes might be supposed to act in the direction of preventing the ions from obtaining the requisite quantity of water. In such circumstances the ions could only obtain sufficient water at the expense of the hydrate of the non-electrolyte, and the final result would depend on whether ion or non-electrolyte was most effective in obtaining water (see Lowry, *Trans. Faraday Soc.*, 1905, **1**, 197). It would also follow that with the increasing concentration of the non-electrolyte the proportion of hydrated non-electrolyte formed would increase, with a corresponding decrease in the hydrated ions. Such an explanation is, however, merely surmise, and does not altogether apply to the strongest non-electrolyte solutions where the water is insufficient to form any hydrate.

EXPERIMENTAL.

The solutions used were made up by weighing both the substance and the water in which it was dissolved. Saturation was obtained by cooling the saturated solution in contact with solid from a somewhat higher temperature to 25° in a thermostat, and by shaking at 25°. The amount of potassium sulphate was determined by direct weighing of the salt after evaporation and ignition, or by estimating the amount of sulphate by means of barium chloride.

The percentage composition of the solutions and the number of molecules of solutes per 1000 molecules of water from which the curves are drawn are as follows:

Aqueous Alcohol—Potassium Sulphate.

Alcohol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Alcohol.	Potassium sulphate.
1·35	9·17	89·48	5·9	10·6
4·80	6·90	88·30	21·3	8·1
7·80	4·96	87·24	35·0	5·9
9·70	4·32	85·98	44·2	5·2
12·34	3·57	84·09	57·4	4·4
14·51	2·71	82·78	68·6	3·4
15·26	2·66	82·08	72·7	3·3
20·50	1·83	77·67	103·2	2·4
26·91	0·97	72·12	146·1	1·4
35·97	0·41	63·62	—	—
43·90	0·22	55·88	—	—
69·26	0·016	30·72	—	—

Aqueous Pyridine—Potassium Sulphate.

Pyridine.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Pyridine.	Potassium sulphate.
4·23	7·95	87·82	11·0	9·4
13·90	4·77	81·33	38·9	6·1
24·51	2·75	72·74	76·8	3·9
34·19	1·47	64·34	121·1	2·4
46·29	0·45	53·26	198·0	0·9
55·93	0·12	43·95	—	—
75·90	0·006	24·09	—	—

Aqueous Ethylene Glycol—Potassium Sulphate.

Ethylene glycol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Ethylene glycol.	Potassium sulphate.
3·16	9·67	87·17	10·5	11·5
9·78	7·69	82·53	34·4	9·6
18·47	5·74	75·79	70·8	7·8
32·11	3·57	64·32	145·0	5·7
49·03	1·83	49·14	289·7	3·8

Aqueous Chloral Hydrate—Potassium Sulphate.

Chloral hydrate.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Chloral hydrate.	Potassium sulphate.
6·44	9·13	84·43	8·3	11·2
9·09	8·41	82·50	12·0	10·5
12·38	7·79	79·83	16·9	10·1
13·20	7·31	79·49	18·1	9·5
22·07	5·88	72·05	33·4	8·4
33·15	4·54	62·31	58·0	7·5
44·40	3·36	52·24	92·6	6·6
47·30	2·92	49·78	103·5	6·1
62·82	2·00	35·18	194·5	5·9
70·28	1·75	27·97	273·8	6·5
80·36	1·40	18·24	—	—
85·26	1·08	13·66	—	—

Aqueous Glycerol—Potassium Sulphate.

Glycerol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Glycerol.	Potassium sulphate.
8·96	8·87	82·17	21·3	11·2
13·36	7·69	78·95	33·1	10·1
20·34	6·47	73·19	54·4	9·1
24·15	5·83	70·02	67·5	8·6
33·73	4·44	61·83	106·8	7·4
40·40	3·65	55·95	141·4	6·7
43·52	3·38	53·10	160·4	6·6
50·18	2·69	47·13	208·4	5·9
57·22	2·07	40·71	275·1	5·3
67·94	1·53	30·53	—	—
78·18	0·98	20·84	—	—
98·28	0·73	0·99	—	—

Aqueous Mannitol—Potassium Sulphate.

Mannitol.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Mannitol.	Potassium sulphate.
3 20	10·32	86·48	3·7	12·3
5·82	10·07	84·11	6·8	12·3
8·35	9·61	82·04	10·1	12·1
11·26	9·19	79·55	14·0	11·9
14·30	8·66	77·04	18·4	11·6
17·22	8·35	74·43	22·9	11·6

Aqueous Sucrose—Potassium Sulphate.

Sucrose.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Sucrose.	Potassium sulphate.
9.56	9.65	80.79	6.2	12.3
18.55	8.65	72.80	13.4	12.3
28.16	7.42	64.42	23.0	11.9
37.24	6.35	56.41	34.8	11.6
47.55	5.21	47.24	52.9	11.4
57.00	4.24	38.76	77.5	11.3

Aqueous Acetone—Potassium Sulphate.

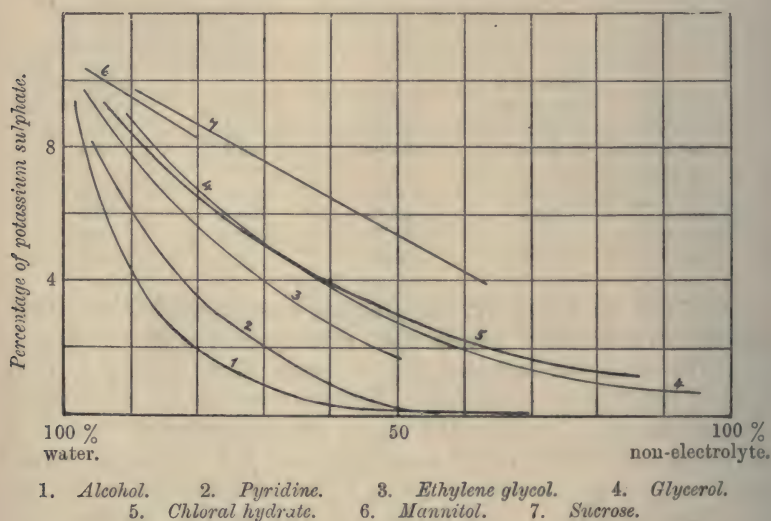
Acetone.	Potassium sulphate.	Water.	Molecules per 1000 molecules of water.	
			Acetone.	Potassium sulphate.
4.92	7.20	87.88	17.4	8.5
10.06	5.02	84.92	36.7	6.1
16.23	2.96	80.81	62.3	3.8
24.31	1.50	74.19	101.7	2.1
37.19	0.47	62.34	185.2	0.8
46.29	0.20	53.51	268.5	0.4
62.40	0.03	37.57	—	—

Certain of the curves (p. 384) require some consideration. Pyridine dissolved in water affords some evidence of the formation of a hydroxide from the fact that it precipitates ferric hydroxide from aqueous solutions of iron salts. When drawn up on the basis of a fixed amount of water, this curve cuts the alcohol curve. It was observed that above the temperature of 45° two liquid phases formed at all concentrations above 5 per cent. and below 46 per cent. approximately. The position of the chloral hydrate curve close to the glycerol curve appears to us to demonstrate that the cause of the depression of solubility is similar in both cases, which does not support the deductions of Jones and Getman (*loc. cit.*) as to the remarkable difference in hydration of these two substances. It will be seen that if the chloral hydrate curve is expressed molecularly with reference to 1000 molecules of water, the end of the curve begins to rise slightly, suggesting that potassium sulphate is soluble in absolute chloral hydrate. An actual determination with liquefied chloral hydrate at 45° gave the solubility as 0.38 per cent. of potassium sulphate.

Glycerol of 99.0 per cent. strength dissolved 0.73 per cent. of potassium sulphate, an amount which is much greater than would be dissolved by the water present. It must be concluded that glycerol also dissolves potassium sulphate.

Both the mannitol and sucrose curves are practically straight lines. In other words, the decrease in the solubility of potassium sulphate in concentrated solutions of these two substances varies directly as the amount of solute present originally, so that the decrease, if due at all to hydration of the solute, requires the same degree of hydration at all concentrations. This is inadmissible on the usual assumption that the degree of hydration depends upon the amount of water. The mannitol curve could not be carried further than the point shown, which is very close to the saturation point of mannitol.

The solubility in aqueous acetone of varying concentrations expressed per 1000 molecules of water gave a curve which followed



the alcohol curve closely, but fell somewhat below it. Acetone was therefore found to possess the greatest precipitating effect of the non-electrolytes examined.

Both pyridine and absolute alcohol dissolve minute quantities of potassium sulphate, but the amount was too small for accurate estimation. Schiff (*Annalen*, 1861, 118, 362) determined the solubility of potassium sulphate in aqueous alcohol at 15°, and gave four points only. This curve, as far as it goes, runs parallel with and a little below the one given here.

It is of interest to compare the curve for solubility in potassium acetate solutions with the foregoing curves. The position occupied is well below the alcohol curve, a result which may be accounted for if to the main action of non-ionised potassium acetate as

precipitant is added the influence of the potassions from the ionised portion.

Hydration of the ions of the salt might be considered as a contributory cause of the depression of solubility. As the rate of decrease is for most of the curves greatest with the dilute solutions, this assumption appears to receive some support; but it cannot be considered quite satisfactory as an explanation, if it is borne in mind that the decrease is continuous even in the strong solutions where there is not sufficient water to form hydrates. Dilute solutions are, however, the limiting cases, and here again we find, as usual, that the rules deduced from the dilute do not apply to concentrated solutions. It is hoped that the results of an investigation now proceeding as to the influence of one non-electrolyte on the solubility of another may throw some light on the possibility of the hydration of ions being a contributory cause of the depression of the solubility of salts by non-electrolytes.

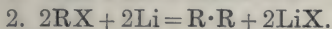
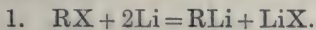
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XLIII.—*The Action of Calcium and Lithium on Organic Halides.*

By JAMES FREDERICK SPENCER and GWYNNEDD MARY PRICE.

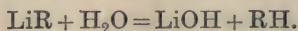
In a previous paper (Spencer and Wallace, Trans., 1908, **93**, 1827) mention was made of a preliminary experiment in which lithium reacted with α -bromonaphthalene with the formation of naphthalene. The present communication describes a series of experiments in which the action of calcium and lithium on organic halogen derivatives has been studied. Lithium reacts with a large number of organic halogen derivatives when the two substances are heated together. In many cases this reaction takes place at the boiling point of the organic compound, but with some substances, notably methyl iodide and bromobenzene, higher temperatures are required, which necessitate the use of sealed tubes. With *isopropyl* iodide and methyl *p*-bromobenzoate, no reaction took place.

The reaction may be regarded as proceeding in the two directions indicated by the equations:



The products obtained in some cases showed that the reaction had proceeded according to equation 1, for example, those obtained

from *p*-bromotoluene, *p*-chlorophenol, *p*-chloroaniline, and *p*-bromoacetanilide, whilst in other cases the products indicated that the reaction had taken place in both directions. None of the reactions investigated proceeded along the direction indicated by the second equation alone. In all cases white, deliquescent compounds were formed, which reacted with water with the evolution of heat and the formation of the parent substance of the halogen derivative employed. The reaction with water can be represented by the equation:



The white, deliquescent compounds obtained, on the basis of the above equations, consist of mixtures of lithium halide and the lithium derivative of the hydrocarbon. It has been found practically impossible to separate these two substances owing to the ease with which the lithio-hydrocarbon is decomposed by solvents and the atmospheric moisture, but an analysis was made of the whole solid product in the case of the reaction between propyl iodide and lithium, and the results point to the presence of lithio-propane.

The yield of the product in these reactions varies considerably, from about 80 per cent. of the theoretical in the case of *m*-chloroaniline to about 8 per cent. in the case of octyl iodide, but generally they are good.

The reaction products, in all experiments where aniline derivatives were employed, had a strong odour of carbylamine, but this substance was not present in quantity large enough to be isolated. The reaction products in the case of *p*-bromoacetanilide contained much aniline, which is attributed to the hydrolysis of the original product, acetanilide, by the lithium hydroxide during the steam distillation.

The reaction between iodobenzene and lithium was also tried in absolute ether solution under the usual Grignard conditions. No compound other than diphenyl and lithium iodide could be isolated from the reaction products, so that it may be taken that lithium and halogen derivatives in ether solution react according to the Wurtz reaction and not according to the Grignard reaction.

Calcium did not react very readily with organic halides, and in those cases where reaction did occur, the products rarely exceeded 40 per cent. of the theoretical amount. The reaction may be regarded as taking place along two lines, analogous to those of the corresponding reactions with lithium and magnesium (Trans., 1908, 93, 69):

1. $\text{Ca} + \text{RX} = \text{R} \cdot \text{CaX}.$
2. $\text{Ca} + 2\text{RX} = \text{CaX}_2 + \text{R} \cdot \text{R}.$

In many cases, although indication of a reaction was given on heating the two substances at the boiling point of the organic halide, it was necessary to employ higher temperatures and pressure to cause the action to proceed to any large extent, and in all such cases a considerable quantity of gas was evolved on opening the sealed tubes. The gases evolved consisted of hydrogen and both saturated and unsaturated open-chain hydrocarbons. The solid products were generally white, crystalline, deliquescent substances of the formula RCaX , which were coloured brown by the products of the pyrogenic decomposition of the organic halide.

The products from the reactions with aniline derivatives always had a strong odour of carbylamine, but this substance was not present in sufficient quantity to be isolated. The intermediate compounds of the formula RCaX were extremely difficult to isolate, but in the case of *p*-chlorophenol it was found possible to isolate and analyse the derivative, which agreed well with the formula $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CaCl}$.

E. Beckmann (*Ber.*, 1905, **38**, 905) states that ethyl iodide and calcium react very readily in ethereal solution, with the formation of the compound $\text{C}_2\text{H}_5\cdot\text{CaI}\cdot\text{O}(\text{C}_2\text{H}_5)_2$, the whole reaction being complete in a few minutes. We have repeated this reaction and also the reaction with iodobenzene under similar conditions, and have obtained in both cases products of the type $\text{R}\cdot\text{CaI}\cdot\text{O}(\text{C}_2\text{H}_5)_2$, but the reaction took place very slowly, requiring about twenty hours for completion. The addition of a trace of iodine accelerated it somewhat, but even then it was much slower than indicated by Beckmann.

Metallic calcium, even in inorganic reactions, is difficult to manipulate owing to the insolubility of its derivatives, which generally coat the metal, and thereby stop or greatly impede the reaction. This probably, in addition to a possible superficial coating of oxide on the metal employed, may be the reason for the difficulty experienced in these experiments, and may also explain the poor yields obtained.

EXPERIMENTAL.

In the experiments with lithium, the metal was cut into small pieces under ether, then quickly dried with filter paper, and added to the organic halide. Equimolecular quantities of the metal and halide were used in all cases. The reactions with all the substances tried, except bromobenzene and methyl iodide, took place when heated in a quartz flask, fitted with a condenser, at the boiling point of the halide for periods varying from three to twenty hours.

The reaction products were in all cases white, crystalline, deliquescent solids, which decomposed on the addition of water

with the evolution of heat. The products, after treatment with water, were distilled in a current of steam, and the distillate and the residue in the distilling flask investigated. The results, together with the yields of the products, are given in the table below. The reaction between lithium and iodobenzene was also carried out in ethereal solution, and the sole product formed was diphenyl in small quantity.

The reactions between lithium and bromobenzene and methyl iodide only took place when heated in sealed tubes for about six hours at 250°. The tubes were then cooled in liquid air and opened, and the gases evolved on warming collected and analysed. The residue was then treated with water, and in the case of methyl iodide further quantities of gas were evolved with the evolution of heat. In the case of bromobenzene, benzene was formed, and this was distilled over in steam:

Reacting substance.	Experimental conditions.	Products.
Iodobenzene.....	Heated 1 hour at 188°	70 per cent. benzene & diphenyl
Bromobenzene.....	Heated in sealed tube at 150° for 8½ hours	Benzene and diphenyl
<i>p</i> -Bromotoluene	Heated 1½ hours at 184°	24 per cent. toluene
<i>p</i> -Chlorotoluene	Heated 4½ hours at 150°	7 per cent. toluene ; <i>p</i> -ditolyl
<i>m</i> -Chloroaniline	Heated ½ hour at 230°	80 per cent. aniline ; <i>m</i> -diamino-diphenyl, traces of carbylamine
<i>p</i> -Chloroaniline	Heated 1½ hours at 230°	68 per cent. aniline, traces of carbylamine
<i>p</i> -Bromoacetanilide.....	Heated 2 hours at 210°	40 per cent. aniline, 12 per cent. acetanilide
<i>p</i> -Chlorophenol	Heated several minutes at 217°	14 per cent. phenol
α -Chloronaphthalene ...	Heated 17½ hours at 263°	Naphthalene ; α -dinaphthyl
Methyl iodide	Heated in a sealed tube for 4½ hours at 200°	27 per cent. ethane, 33 per cent. methane mixed with 40 per cent. hydrogen
<i>n</i> -Propyl iodide	Heated 1½ hours at 46·5°	<i>n</i> -hexane ; <i>n</i> -propane
<i>sec</i> .-Octyl iodide	Heated 20 hours at 220°	9 per cent. octane ; 17 per cent. hexadecane, <i>m. p.</i> 20°

The calcium used in these experiments was the rasped variety supplied by Kahlbaum; it was quite bright and metallic-looking in appearance, but occasionally had a slightly bluish tinge, which may have been due to a superficial coating of oxide. The reactions were first tried at the boiling point of the organic substance used, and as in no case did the reaction proceed to a marked extent, they were then carried out in sealed tubes at temperatures varying from 160° to 250°. The substances were mixed in equimolecular quantities. After cooling, the tubes were immersed in liquid air and opened. No gas was evolved on opening, but on warming to

the atmospheric temperature, gas was evolved, which consisted mainly of hydrogen with small quantities of methane, acetylene, and carbon dioxide. This indicates that calcium, like magnesium (Trans., 1908, **93**, 1823), has the property of absorbing large quantities of hydrogen at low temperatures. The solid products were then cautiously treated with water, and any gas evolved was collected and analysed. The aqueous mass was then distilled in a current of steam, and the products, indicated in the table below, collected. The crystalline product of the reaction between *p*-chlorophenol was pressed on a porous plate and then washed with small quantities of absolute ether to remove any unchanged chlorophenol, dried, and analysed:

Found, $\text{Ca} = 23.1$.

$\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CaCl}$ requires $\text{Ca} = 23.7$ per cent.

The lower alkyl halides reacted with calcium when heated at 250° in a sealed tube, but the products could not be obtained, owing to the bursting of the tubes. No matter what precautions were taken, the tubes always burst after they had been heated for about one hour, indicating that a violent reaction had suddenly taken place.

The following table gives a brief summary of the reactions carried out and their products:

Reacting substance.	Experimental conditions.	Products.
Iodobenzene	Heated in a sealed tube at 200° for 16 hours	40 per cent. benzene; 2 per cent. diphenyl
<i>p</i> -Chloroaniline.....	Heated in a sealed tube at 155° for 14 hours	31.5 per cent. aniline
<i>p</i> -Chlorophenol.....	Heated in a sealed tube at 160° for $12\frac{1}{2}$ hours	36 per cent. phenol
<i>p</i> -Bromoacetanilide	Heated in a sealed tube at 200° for 15 hours	Small quantities of aniline and acetanilide, with a trace of carbylamine

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XLIV.—*The Influence of Radium Emanation on Equilibrium in a Gaseous System.*

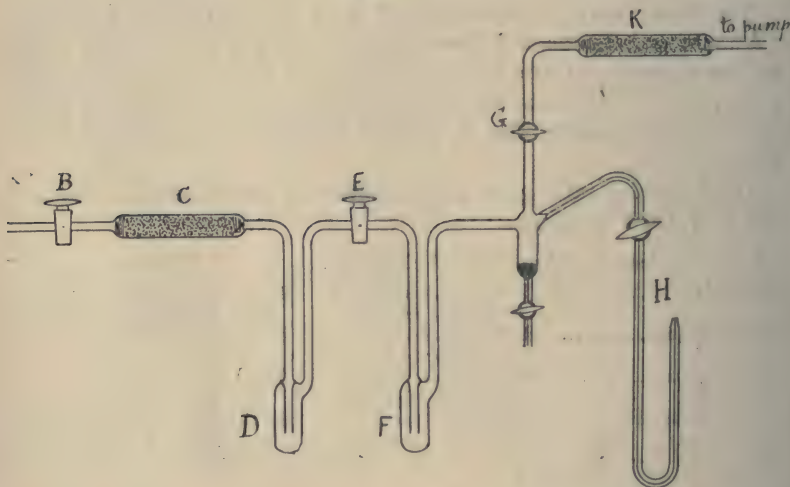
By FRANCIS LAWRY USHER.

SOME interesting deductions concerning the nature of chemical change induced by radium emanation have lately been recorded by Cameron and Ramsay (Trans., 1908, **93**, 966) as the result of quantitative experiments on the decomposition of water, ammonia, hydrogen

chloride, and the oxides of carbon, and on the combination of hydrogen and oxygen and nitrogen and hydrogen in presence of the emanation.

The principal conclusions drawn by these authors are (1) that the changes observed are due almost entirely to the α -particles, and (2) that each particle of emanation in disintegrating produces, *ceteris paribus*, the same amount of change. The experiments described are regarded by the authors as preliminary, and the results have qualitative rather than quantitative significance. At the suggestion of Sir William Ramsay, the investigation to be described in this paper was undertaken with the object of obtaining a more definite knowledge of the mechanism of chemical change produced by the emanation,

FIG. 1.



based on an accurate study of the course of some simple reaction. For this purpose, five series of observations have been made, three with pure dry ammonia, and two with a mixture of hydrogen and nitrogen of the composition $3\text{H}_2 + \text{N}_2$.

EXPERIMENTAL.

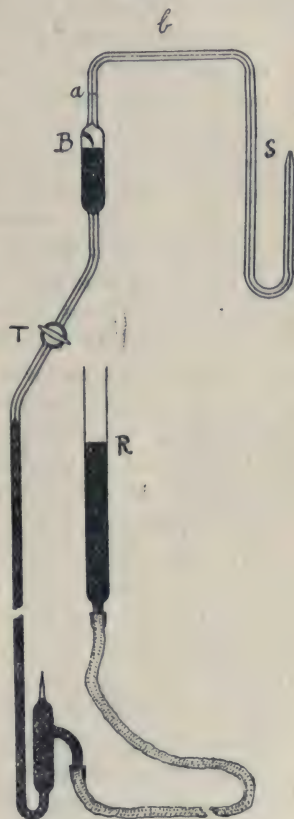
It will be convenient to describe in detail the method of procedure in the two cases. Fig. 1 represents the apparatus used for the experiments with ammonia. In the first place the tap B was closed, and the whole apparatus exhausted by means of a small mercury pump. Ammonia, prepared from pure ammonium chloride and sodium hydroxide, was then introduced through B and condensed in the

vessel *D*, which was surrounded with liquid air. *B* was again closed, and the apparatus once more exhausted in order to remove traces of air. The liquid air was removed from *D*, which now contained pure ammonia, and a convenient quantity of this (about 1 c.c.) was pumped off and collected over mercury in a carefully dried gas-tube. *D* was once more cooled with liquid air, so as to condense the ammonia remaining in the apparatus, the tap *E* was closed, and the system on the pump side of *E* thoroughly exhausted.

Radium emanation, accumulated during four or five days from a solution containing 0.2111 gram of metallic radium, and mixed with about 0.5 c.c. of hydrogen, was now introduced through the capillary syphon *H*, and *F* was then surrounded with liquid air. After about fifteen minutes, in which time all the emanation had condensed, the hydrogen was removed through the pump, and the required quantity of ammonia, prepared in the way described, was introduced through *H* and frozen in *F* on top of the condensed emanation. If the pump was worked at this stage, traces of gas continued to pass over indefinitely, and an analysis of the gas thus collected showed it to consist solely of hydrogen and nitrogen, so that it appears that solid ammonia is decomposed by the emanation, even at -190° . The drying tubes, *C* and *K*, contained lime freshly prepared from marble. The mixture of ammonia and emanation was next introduced into the apparatus shown in Fig. 2. This consisted essentially of a short length (about 5 cm.) of glass tubing of 1 cm. bore, containing an opaque glass point sealed in so as to form a constant-volume gas chamber, *B*, the

volume contained between a mercury surface set to the point and a mark, *a*, on the capillary stem being previously accurately determined by calibration with mercury. The constant-volume chamber terminated above in a capillary syphon, *S*, and at its lower end was sealed to a piece of narrower glass tubing about 80 cms. long, including a stop-cock, *T*, the only one used in the apparatus, which was permanently below the mercury surface and never came into

FIG. 2.



contact with the gas. A mercury reservoir, *R*, of the same diameter as the chamber *B*, was connected with the apparatus by a length of rubber pressure tubing. The greatest care was taken to dry the inner glass surface thoroughly, and for this purpose, before the stop-cock was greased, the entire apparatus was placed in a large air-oven and kept at a high temperature for several hours while a current of dried air was passed through it. In order to introduce the gas, the apparatus was filled with pure dry mercury, and the tube containing the gas was brought over the end of the syphon, *S*, in a mercury trough. By lowering the reservoir, *R*, the gas was admitted, and the end of the mercury thread which followed it was set to the mark *a* on the capillary tubing. The thread was then frozen in the horizontal portion of the capillary at *b* by means of a paper-cup containing solid carbon dioxide, and the tip of the syphon was then sealed with a small blowpipe flame. Finally, the apparatus was fixed up against a glass scale ruled in millimetres, and frequent readings were taken of the pressure exerted by the gas when the mercury surface was set exactly to the point. During the interval between each successive reading, the tap *T* was closed, so that the reaction proceeded at constant volume. It happened, on a few occasions, that after the capillary tip had been sealed and the mercury thread had thawed, the latter was no longer set exactly to the mark *a*, and in such cases the distance between the two was measured and a correction on the volume was made, as the capillary had previously been calibrated by weighing out mercury. In making a reading the temperature of the gas and of the mercury column was carefully noted, and the barometric height was read at the same time.

The above description refers to the experiments with ammonia, but those with nitrogen and hydrogen were carried out in exactly the same manner. The gases were obtained by sparking pure ammonia over mercury in a glass tube. The undecomposed ammonia was removed with a few drops of phosphoric acid, the residual mixture of nitrogen and hydrogen was carefully dried, and a convenient quantity was collected in a tube in the same way as the ammonia, the calcium oxide, however, being replaced by phosphoric oxide. The subsequent procedure differed slightly from that employed in the experiments with ammonia. The apparatus shown in Fig. 1 was modified to some extent, but it will suffice here to say that, after thorough exhaustion of the apparatus through the mercury pump, the previously dried emanation, accompanied by its excess hydrogen, was taken in through a capillary syphon, the emanation was frozen with liquid air, and the hydrogen removed through the pump. Finally, the liquid air was removed, and the sample of nitrogen and hydrogen collected for the experiment was admitted and allowed to mix with

the emanation, the mixture being then pumped off and transferred to one of the reaction vessels already described.

It will be obvious that throughout the whole of the operations just described there is no possibility of serious contamination. It is true that during the process of purification, gaseous emanation was brought into contact with the stop-cocks *H*, *G*, and *E* (Fig. 1), but the total time of contact between tap grease and emanation was certainly less than thirty minutes, and it was proved by a blank experiment with emanation and some of the same rubber tap grease that if oxygen is excluded, the only gaseous product of the action is pure hydrogen, the amount of which produced in half an hour would be quite negligible.

Each experiment was allowed to proceed for at least four weeks, at the end of which period the amount of emanation still present was insignificant. During the first two days, readings were taken every few hours, and afterwards at the rate of about one every twenty-four hours.

At the conclusion of each experiment, the gas was removed from the reaction vessel and analysed, the ammonia, nitrogen and hydrogen, and gases absorbable by potassium hydroxide being determined. Reference will be made to those analyses in the discussion of the results.

Experiment I.—Volume of reaction chamber: 2.1187 c.c. Initial volume of ammonia at 0° and 760 mm. = 0.4514 c.c. About half the quantity of emanation taken for this experiment was accidentally lost, so that the proportion of ammonia to emanation is not known :

Time in days.	Corrected vol. of gas.	Volume increment.	$1/\log V_0/V_t$	$1/E_t \log V_0/V_t$
0.0	0.4514	0.0	—	—
0.56	0.4801	0.029	0.0516	0.0571
0.77	0.4920	0.041	0.0538	0.0620
1.56	0.5183	0.067	0.0448	0.0594
1.83	0.5235	0.072	0.0413	0.0571
2.58	0.5436	0.092	0.0384	0.0615
4.54	0.5765	0.125	0.0301	0.0707
5.54	0.5838	0.132	0.0272	0.074
7.56	0.5956	0.144	0.0221	0.086
9.67	0.6020	0.151	0.0183	0.103
12.58	0.6048	0.153	0.0143	0.137
40.00	0.627	0.176	0.0054	—

Experiment II.—Volume of reaction chamber: 3.1655 c.c. Initial volume of ammonia at 0° and 760 mm. = 1.843 c.c. Initial pressure = 474 mm.:

Time in days.	Corrected vol. of gas.	Volume increment.	$1/t \log. V_o/V_t.$	$1/E_t \log. V_o/V_t.$
0.0	1.843	0.0	—	—
0.042	1.854	0.011	0.0619	0.0623
0.083	1.871	0.028	0.0801	0.0812
0.104	1.874	0.031	0.0708	0.0720
0.135	1.881	0.038	0.0670	0.0685
0.191	1.891	0.048	0.0601	0.0621
0.865	2.068	0.225	0.0654	0.0764
1.031	2.104	0.261	0.0643	0.0777
1.198	2.145	0.302	0.0649	0.0808
1.854	2.262	0.419	0.0605	0.084
2.042	2.302	0.459	0.0610	0.088
2.185	2.323	0.480	0.0600	0.089
2.840	2.416	0.573	0.0570	0.095
3.230	2.455	0.612	0.0543	0.097
3.840	2.512	0.669	0.0510	0.102
3.958	2.523	0.680	0.0505	0.103
5.840	2.652	0.809	0.0430	0.123
6.896	2.703	0.860	0.0396	0.136
7.840	2.724	0.881	0.0360	0.147
8.840	2.757	0.914	0.0337	0.165
9.840	2.775	0.932	0.0311	0.183
12.886	2.804	0.961	0.0248	0.253
36.000	2.871	1.028	0.0098	—

Experiment III.—Volume of reaction chamber: 2.406 c.c. Initial volume of ammonia at 0° and 760 mm. = 0.909 c.c. Initial pressure = 306 mm.:

Time in days.	Corrected vol. of gas.	Volume increment.	$1/t \log. V_o/V_t.$	$1/E_t \log. V_o/V_t.$
0.0	0.909	0.0	—	—
0.031	0.914	0.005	0.0772	0.0776
0.073	0.923	0.014	0.0923	0.0934
0.76	1.037	0.128	0.0868	0.1000
1.08	1.083	0.174	0.0855	0.103
1.75	1.154	0.245	0.0779	0.108
2.08	1.188	0.279	0.0766	0.110
2.78	1.237	0.328	0.0700	0.116
3.75	1.291	0.382	0.0632	0.124
4.75	1.325	0.416	0.0559	0.132
6.75	1.377	0.468	0.0466	0.156
7.76	1.387	0.478	0.0418	0.168
8.75	1.397	0.488	0.0382	0.184
9.75	1.401	0.492	0.0347	0.202
10.76	1.408	0.499	0.0321	0.221
11.76	1.419	0.510	0.0304	0.253
13.77	1.419	0.510	0.0260	0.310
14.76	[1.440]	[0.531]	[0.0258]	[0.359]
15.76	1.419	0.510	0.0227	0.392
32.00	1.433	0.524	0.0117	—

Experiment IV.—Nitrogen and hydrogen. Same tube as in Exp. I. Initial volume of mixed gases at 0° and 760 mm. = 1.602 c.c. Initial pressure = 615 mm. :

Time in days.	Corrected vol. of gases.	Volume increment.
0.0	1.602	0.0
0.135	1.585	-0.017
0.698	1.540	-0.062
2.698	1.462	-0.140
2.990	1.460	-0.142
3.678	1.442	-0.160
4.010	1.441	-0.161
4.698	1.425	-0.177
11.80	1.403	-0.199
31.89	1.362	-0.240

Experiment V.—Nitrogen and hydrogen. Same tube as in Expt. II. Initial volume of mixed gases at 0° and 760 mm. = 2.323 c.c. Initial pressure = 594 mm. :

Time in days.	Corrected vol. of gases.	Volume increment.
0.0	2.323	0.0
0.7	2.273	-0.050
1.7	2.247	-0.076
2.7	2.230	-0.093
4.7	2.241	-0.082
5.7	2.228	-0.095
6.7	2.225	-0.098
30.0	2.181	-0.142

The analysis of the gases at the conclusion of each experiment was carried out by means of a small glass burette, provided with a stop-cock and capillary syphon, and containing six opaque glass points. The volume between a mercury surface set to each of these points and a mark on the capillary stem was accurately determined by calibration with mercury, and measurements were made by observing, against a glass scale, the difference between the level of the mercury in a reservoir connected with the burette and that of the mercury set exactly to one or other of the points. The measurements are in all cases correct to within 0.002 c.c. The gas was always measured dry, and was, if necessary, for example, after explosion or treatment with a wet reagent, pumped through a small tube of phosphoric oxide. Ammonia was determined by absorption with a few drops of phosphoric acid, hydrogen by explosion with a measured excess of oxygen, and carbon dioxide by absorption with a lump of fused and moistened potassium hydroxide.* The residual gas, after removal of excess oxygen by phosphorus, was measured and considered to be nitrogen. The treatment of the gases with liquid and solid reagents took place in small gas tubes, the gas being completely freed from the reagent

* Any other acid gases, oxides of nitrogen, etc., are consequently called "CO₂."

and dried before introduction into the measuring burette. The following table gives the results of the analyses of the gases at the termination of the experiments:

	I.	II.	III.	IV.	V.
	c.c.	c.c.	c.c.	c.c.	c.c.
NH ₃	0.173	0.78	0.312	0.006	0.010
H ₂	0.327	1.56	0.814	0.980	1.321
N ₂	0.121	0.56	0.298	0.356	0.669
CO ₂	0.002	0.014	0.000	0.019	0.185
CO	0.004	0.004	0.009	0.001	0.003

Discussion of Results.

It is interesting to compare these results with the figures given by Cameron and Ramsay, and for this purpose it is convenient to calculate the values of the expression: $Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$ and the corresponding logarithms, as is done by these authors. These values are given in the following table for Expts. I and III; the reasons for omitting Expts. II, IV, and V will be given presently.

EXPERIMENT I.

Time in days.	$V_{\infty} - V_t$.	$Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$.	Log. Q .	Log. $Q/100/t = -k$.
0.00	0.176	100.0	2.000	—
0.56	0.147	83.6	1.922	1.392
0.77	0.135	76.8	1.885	1.494
1.56	0.109	62.0	1.792	1.334
1.83	0.104	59.1	1.772	1.245
2.58	0.084	47.7	1.679	1.243
4.54	0.051	29.0	1.462	1.185
5.54	0.044	25.0	1.398	1.086
7.56	0.032	18.2	1.260	0.979
9.67	0.025	14.2	1.152	0.877
12.58	0.023	13.1	1.117	0.702

EXPERIMENT III.

Time in days.	$V_{\infty} - V_t$.	$Q = 100 \frac{V_{\infty} - V_t}{V_{\infty} - V_0}$.	Log. Q .	Log. $Q/100/t = -k$.
0.00	0.524	100.0	2.000	—
0.76	0.396	75.6	1.878	0.161
1.08	0.350	66.8	1.825	0.162
1.75	0.279	53.3	1.727	0.156
2.08	0.245	46.8	1.670	0.159
2.78	0.196	37.4	1.573	0.154
3.75	0.142	27.1	1.433	0.151
4.75	0.108	20.6	1.314	0.144
6.75	0.056	10.7	1.029	0.144
7.76	0.046	8.8	0.944	0.136
8.75	0.036	6.9	0.839	0.133
9.75	0.032	6.1	0.785	0.125
10.76	0.025	4.8	0.681	0.123
11.76	0.014	2.7	0.431	0.133
13.77	0.014	2.7	0.431	0.114

The figures in the last column of the preceding tables represent the constant in the equation $\frac{V_{\infty} - V_t}{V_{\infty} - V_o} = e^{-kt}$, or, rather, the constant calculated with common instead of Napierian logarithms. It will be noticed that the value of $-k$ diminishes fairly regularly with time, and that the underlying assumption, which would require it to remain really constant, does not, therefore, strictly represent the facts.

The time of half action is in Expt. I, 2.4 days, and in Expt. III, 1.9 days, both considerably less than the half-life period of the emanation, which is 3.86 days (Sackur). It seems, therefore, that the simple hypothesis that each atom of emanation in decaying produces the same amount of change, that, in fact, the effect is at any time proportional to the amount of emanation present, although it may be true under certain conditions, requires some modification to make it agree with the experiments here recorded.

Let us assume that the velocity of reaction at any time, t , is proportional, both to the amount of emanation and of ammonia present at that time. Then $-\frac{dv}{dt} = kE_t V_t = KE_t V_t$. Now, during a very small space of time, E_t is constant, so that the above expression can be integrated by keeping KE_t as the constant, and the resulting expression can be subsequently corrected for the variation of E_t . We get then: $\frac{1}{t} \log \frac{V_o}{V_t} = KE_t$.

For the sake of comparison, we may consider that the velocity of decomposition depends only on the amount of ammonia present, and is not influenced by the decay of the emanation. We should then find that $\frac{1}{t} \log \frac{V_o}{V_t}$ was constant. The reaction has been treated as an irreversible unimolecular one, since it is obvious from the analysis of the gases at the end of Expts. IV and V that recombination takes place to an almost inappreciable extent. Whereas in Expt. III, 65.7 per cent. of the ammonia put in was decomposed, in Expt. IV, starting with nitrogen and hydrogen, only 0.75 per cent. of the mixture was recombined.

The values of $\frac{1}{t} \log \frac{V_o}{V_t}$ and of $\frac{1}{E_t t} \log \frac{V_o}{V_t}$ have already been tabulated for Expts. I to III on pp. 393, 394, and it is interesting to note that while the constant becomes smaller with time when no correction for the decay of the emanation is applied, it becomes larger when the correction is introduced. Obviously, it is unreasonable to omit the correction for decay of the emanation; nevertheless, when the full correction is put in, the constant changes in the opposite direction, although at the same time a distinct improvement is noticeable. It

is here suggested that a third factor, namely, the *efficiency* of the emanation, is required in order to explain the increase of the velocity constant with time. Since an α -particle is effective over a range of about 8 cm. in ammonia gas under the pressures employed in these experiments, a large proportion of its energy must be wasted when it is enclosed in a tube of 1 cm. bore, although this waste need not be proportionately greater at one time than another; but one atom of emanation is capable, as will be shown later, of decomposing at least 134,000 molecules of ammonia. It is, therefore, highly probable than when, as in Expt. III, the emanation is present in the proportion of 1 atom to 10,850 molecules of ammonia, the efficiency of an α -particle will be greater, as its chance of colliding with a larger number of molecules increases; in other words, each α -particle will do more work when there is more work to do.

It is possible to make an approximate correction by assuming that the efficiency is proportional to the ratio of the number of emanation molecules to ammonia molecules at any time, although of course this cannot be expected to hold over an extended period.

We may assume that $-\frac{dv}{dt} = KE_t V_t \beta_t$, where β_t is the efficiency.

Then if $\beta_t \propto \frac{V_t}{E_t}$, we get $\frac{1}{V_t t} \cdot \log \frac{V_o}{V_t} = \text{constant}$. This expression gives a much better value for K over a period of six or seven days, starting at one day from the commencement of the experiment, but it afterwards becomes smaller again, a result which is to be expected for two reasons: first, because the assumed correction is the most drastic possible, and can only be strictly valid over a very short range; and secondly, because as the reaction proceeds, the energy of the emanation is more and more used up in useless work, namely, in imparting increased velocity to the accumulating products of decomposition. We can, therefore, make the further assumption [that the efficiency is proportional, not only to the ratio of the amounts of emanation and ammonia, but also to the actual quantity of ammonia present. In this case,

$$\beta_t = \frac{V_t}{E_t} \cdot V_t, \text{ and the velocity constant becomes } K = \frac{1}{\sqrt{E_t V_t} \cdot t} \cdot \log \frac{V_o}{V_t}.$$

The constants calculated in the two ways suggested are tabulated on p. 399 for Expt. III.

The correction appears to be rather too great in the first case, and slightly too small in the second, but on the whole both sets of constants are much better than when no correction for change in efficiency is introduced. It would doubtless be possible by suitably compromising between the two methods to obtain a still more constant value of K , but is it probably not worth while to attempt this, because there are

Time in days.	$K = 1/V_t \log. V_o/V_t$	$K = \frac{1}{\sqrt{E_t V_t t}} \cdot \log. V_o/V_t$
0.073	0.103	0.098
0.76	0.111	0.106
1.08	0.116	0.109
1.75	0.117	0.111
2.08	0.121	0.116
2.78	0.120	0.118
3.75	0.120	0.121
4.75	0.113	0.121
6.75	0.106	0.129
7.76	0.097	0.127
8.75	0.091	0.127
9.75	0.083	0.128
10.76	0.078	0.134
11.76	0.076	0.138

slight complications in all the experiments, and these will now be considered.

It will have been noticed in Expt. IV that if the amount of nitrogen and hydrogen recombined is calculated from the observed change of pressure, there should be 0.240 c.c. of ammonia at the conclusion of the experiment. As a matter of fact, the analysis shows that only 0.006 c.c. was formed. The gases and the apparatus were both very carefully dried, there was no contamination by air, and no possibility of leakage during the course of the experiment; the gas was under considerably reduced pressure the whole time. Clearly, then, nearly a quarter of a c.c. of gas had ceased to exert any pressure. We can make up a balance sheet with respect to the total quantity of hydrogen and nitrogen put in at the commencement, and found at the termination, of two typical experiments: Nos. III and IV, reckoning as hydrogen and nitrogen these gases in combination as well as free. This balance sheet gives the clue to the observed discrepancies.

	Hydrogen put in at commencement.	Nitrogen put in at commencement.	Hydrogen found at end.	Nitrogen found at end.
	c.c.	c.c.	c.c.	c.c.
Expt. III	1.363	0.454	1.282	0.454
„ IV	1.201	0.400	0.989	0.359
Hydrogen lost in Expt. III			0.081 c.c.	
Nitrogen „ „ III			0.000 „	
Hydrogen „ „ IV			0.212 „	
Nitrogen „ „ IV			0.041 „	

In Expt. III a small quantity of nitrogen was probably lost, for the first reading was made as soon as possible after, but not at precisely the same moment as, the emanation was mixed with the ammonia. The initial volume therefore refers to a mixture of ammonia with a trace of its decomposition products, and not to pure ammonia, as is assumed for the purpose of the above calculation.

In Expt. IV we find, as one would expect, that a larger proportion of hydrogen and nitrogen is missing, because the partial pressure of these gases is considerably higher than in the preceding experiment, in which no free hydrogen or nitrogen was introduced initially. Now this missing gas can only have disappeared in three ways: (1) it may have reacted chemically with the glass of which the apparatus was made; (2) it may have been driven into the walls of the vessel and remained there, or (3) it may have gone completely through the glass. The first possibility is very unlikely, because nitrogen was lost as well as hydrogen, and the glass did not present the appearance of having been attacked; only the usual brownish-violet coloration was observed.

In order to settle this question definitely, it was decided to carry out a blank experiment with pure hydrogen and emanation, arranged so that any loss of gas could be observed and measured, and so as to detect any gas which might pass right through the glass. In the meantime, the three reaction chambers employed in the five experiments already described were coarsely powdered, placed in a piece of Jena glass tubing, first exhausted cold by a Töpler pump, and finally heated to redness and again exhausted; nearly 2 c.c. of gas were pumped out of the heated glass, and its composition was as follows. The measured total volume was 1.817 c.c.:

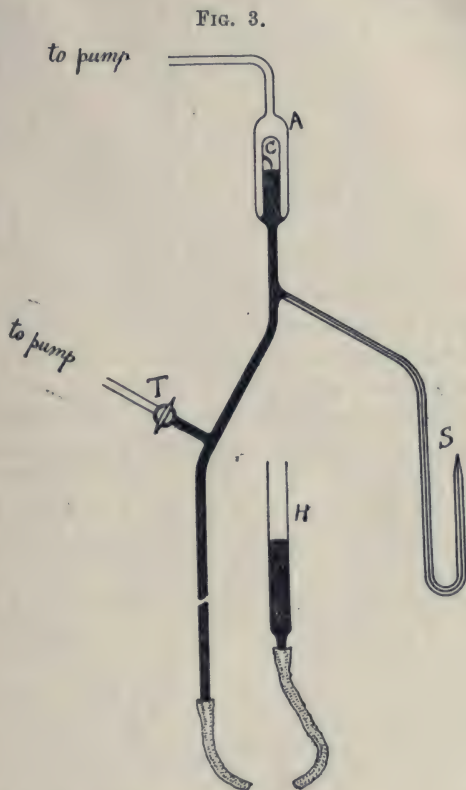
CO ₂	1.416 c.c.
CO	0.240 "
H ₂	0.096 "
N ₂	0.066 "
Total	... 1.818 c.c.

The experiment was rather unsatisfactory, as the powdered glass was not treated with chromic acid to remove traces of grease, dust, etc., before being heated; nevertheless, nearly 0.1 c.c. of hydrogen was recovered, and a rather smaller quantity of nitrogen.

The apparatus used for the blank experiment was made of glass of about the same thickness as that used in the previous experiments. It is diagrammatically sketched in Fig. 3. The constant volume chamber, *C*, containing an opaque glass point, was itself sealed into a wider piece of glass tubing, *A*, which was drawn out at the top and connected, through a small phosphoric oxide tube, with a Töpler pump, no taps being used. The space between the reaction chamber and this outer tube was at the commencement of the experiment very thoroughly evacuated, and the pump with which it was connected was worked from time to time during the experiment in order to collect any gas which might be driven through from the reaction chamber,

The latter was sealed, immediately below the inserted join, to a piece of narrower glass tubing about 80 cms. long, the lower end of which was connected through an air-catch with a length of rubber pressure tubing attached at its distal end to a mercury reservoir, *H*. A small capillary syphon, *S*, was sealed on shortly below the inserted join, and was used for taking in the hydrogen and emanation. Another piece of tubing was sealed on about 4 cms. below the syphon, and was connected through the tap *T'* with a second Töpler pump.

Mercury was first poured into the reservoir, and the rubber tubing was clipped when the mercury stood a short distance below the T-piece carrying the tap *T*. The end of the capillary syphon was sealed, and the apparatus was then very thoroughly exhausted through *T*. The latter was then shut, and the reservoir was raised until the mercury stood in the tubing between the lower T-piece and the capillary syphon. The end of the latter was then scratched with a glass knife, and the point was broken off inside a small



gas tube containing the emanation mixed with about half a c.c. of hydrogen, carefully purified and dried. The gas entered the apparatus, and the reservoir was again raised, until the hydrogen and emanation were forced up into the reaction chamber, and the mercury in the reservoir was level with the tip of the capillary syphon; the latter was then sealed in a blow-pipe flame. The entire apparatus was fixed up in front of a glass scale, and frequent readings were taken of the pressure of the gas when the mercury was set to the point. The volume of the reaction chamber was subsequently determined by measuring the pressure of a quantity of dry air introduced into it, and afterwards

removed and re-measured in a constant-volume point burette already calibrated.

Throughout this experiment no gas passed through the walls of the reaction chamber into the surrounding vacuous space, which remained quite empty. The amount of hydrogen in the tube decreased, however, from 0.610 c.c. to 0.487 c.c. The following table gives the readings:

Time in days.	Corrected vol. of hydrogen.	Volume decrease.	$K=1/E_t.t \log. V_o/V_t.$
0.00	0.573	—	—
1.15	0.530	0.043	0.0363
1.81	0.514	0.059	0.0355
2.81	0.507	0.066	0.0315
3.81	0.510	0.063	0.0261
4.81	0.505	0.068	0.0270
6.81	0.495	0.078	0.0313
8.81	0.494	0.079	0.0360
15.81	0.490	0.083	0.0711
25.81	0.489	0.084	0.267

The results are not sufficiently regular to admit of their application as quantitative corrections to the experiments with ammonia and with nitrogen and hydrogen. It is even possible that after some time the glass walls of the containing vessel become so pitted by the bombardment that the surface is appreciably altered, and, in any case, the problem is probably much more complicated than it at first appears.

At the conclusion of this last experiment, the reaction chamber was powdered, and the powder was carefully cleared with hot chromic acid, washed, dried, and put in a clean Jena-glass tube and exhausted cold. It was then exhausted at a red heat, and in this way 0.076 c.c. of gas was extracted. Its composition was:

CO ₂	0.014 c.c.
H ₂	0.061 „
Total	0.075 „

There can therefore be no doubt that hydrogen, and, to a smaller extent, nitrogen, is driven into the glass walls of its containing vessel when mixed with radium emanation. The greater part of such gas can be recovered when the glass is strongly heated.

In calculating the velocity constants and the values of the expression Q , it was stated on p. 396 that the reasons for omitting Expts. II, IV, and V would be given later. IV and V were of course omitted because the observed pressure changes do not really indicate recombination of nitrogen and hydrogen, as has just been shown. It will be seen on referring to the analysis of the gas from Expt. II that, although there is an *apparent* loss of

hydrogen, there is more nitrogen at the end than there was at the beginning, and the same is true for Expt. V. There was no ordinary leakage during either of these experiments, but the same apparatus was used for each, and this curious result may be explained on the hypothesis that there were bubbles in the glass vessel at its junction with the capillary tubing at its upper end, and that the glass was so thin in the region of these bubbles as to become perforated by the α -particles, and so allowed a slow diffusion of air from without. Unfortunately, the discrepancy was not discovered until after the tubes had been ground up.

Chemical Efficiency of the Emanation.

It has been pointed out that in all the experiments hitherto described, the emanation probably brings about only a fraction of the amount of decomposition which it could effect under more favourable conditions. In Expt. III the total volume of ammonia decomposed was 0.597 c.c., and the emanation which was mixed with it was the product of six days' accumulation, and therefore, according to the recent work of Gray and Ramsay (*Trans.*, 1909, **93**, 1073), 0.000081 c.c. In this experiment, then, the ratio of the volumes of emanation and ammonia was 1 to 7380, or, in other words, each atom of emanation decomposed on the average 7380 molecules of ammonia.

In order to get some idea of the amount of chemical work which could be done by the emanation under favourable conditions, an experiment similar to those described above was carried out on a much larger scale. A large round-bottomed flask of 2 litres capacity was filled with ammonia at about 260 mm. pressure, and mixed with six days' accumulation of emanation. The course of the reaction could not, of course, be followed, but, at the end of a month, the gases were pumped out and the quantity of nitrogen and hydrogen produced was roughly estimated. It was found that 10.9 c.c. of ammonia had been decomposed. This is, in every sense, a minimum value, for no account is taken of the fact that that portion of the emanation which was near the walls of the flask was not entirely used up in decomposing ammonia, and no correction is introduced for gas driven into the glass.

There is, however, no doubt that the conditions of this experiment were extremely favourable as compared with those of the preceding ones, and were probably such as to secure at least 90 per cent. of the maximum amount of decomposition. In this case, one molecule of emanation decomposed 134,300 molecules of ammonia.

If we take this as an approximate measure of the chemical efficiency

of the emanation, we can calculate the fraction of the total energy of the emanation which is used in effecting chemical decomposition.

It is reasonable to assume that the α -particles are mainly responsible for the effects observed, and, further, that their power to decompose ceases when they no longer produce any other physical effect, that is, when their velocity is reduced to 64 per cent. of their average initial velocity of projection.

On this hypothesis, the total kinetic energy of one atom of emanation available for chemical work will be that of three α -particles, since the atoms of radium-*A*, -*B*, and -*C* are projected with less than the critical velocity.

Now, the total kinetic energy of one α -particle is 6×10^{-6} ergs., hence the energy available for chemical work $= (6 \times 10^{-6}) \times (0.64)^2 =$ about 2.5×10^{-6} ergs.

Therefore one atom of emanation produces about 7.5×10^{-6} ergs. available energy. Taking the mechanical equivalent of heat as 4.182×10^7 ergs. per calorie, this amounts to

$$\frac{7.5 \times 10^{-6}}{4.182 \times 10^7} = 1.8 \times 10^{-13} \text{ calories.}$$

Now, 134,300 molecules of ammonia (which are decomposed by one atom of emanation) require for complete decomposition about 2.02×10^{-15} calories, hence the chemical efficiency of the α -particle in this experiment is

$$\frac{2.02 \times 10^{-15}}{1.8 \times 10^{-13}} = 1.12 \times 10^{-2},$$

or a little more than 1 per cent.

As regards its influence on equilibrium in the system ammonia-hydrogen-nitrogen, it can only be said that if any definite state of equilibrium were reached under ideal conditions, it would be one corresponding with a very high temperature. Under ordinary conditions there is no true equilibrium, but only a state of rest depending on the proportions of ammonia and emanation, surface, and possibly other factors as well. The emanation cannot be called a catalyst in any sense, and the effects produced are probably mechanical or electrical in origin.

The principal conclusions arrived at in the course of this investigation may be summarised as follows :

(1) Ammonia is decomposed by radium emanation at the ordinary temperature, and the decomposition is nearly irreversible.

(2) Recombination was not observed to take place to a greater extent than 0.86 per cent.

(3) Decomposition of solidified ammonia by solidified emanation proceeds with appreciable velocity at -190° .

(4) The decomposition at the ordinary temperature follows approximately the course of a unimolecular homogeneous reaction when correcting factors for the decay of the emanation and alteration of its efficiency with time are introduced.

(5) If the ratio of ammonia to emanation molecules does not exceed 10,000 to 1, the statement that each atom in disintegrating produces the same effect is not strictly true, on account of the waste involved when the system is rich in emanation.

(6) The largest effect observed was the decomposition of 134,300 molecules of ammonia per atom of emanation.

(7) The energy required to produce the largest effect observed was about 1 per cent. of the energy actually expended during the production of that effect.

(8) All experiments with gases in glass vessels in presence of the emanation are complicated by the fact that gas is driven into the glass, and can only be recovered by heating strongly.

(9) Hydrogen is driven into glass to a greater extent than nitrogen, and as much as 0.24 c.c. of the former gas has been thus lost during a single experiment.

I wish, in conclusion, to express my indebtedness to Sir William Ramsay, who kindly placed at my disposal the emanation used in the experiments, and whom I have also to thank for his advice and criticism.

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XLV.—*Attempted Resolution of Racemic Aldehydes.*

By WILLIAM ORD WOOTTON.

DURING recent years numerous investigations have been undertaken with a view to elucidating the relationship between the chemical composition and rotatory power of optically active substances. Although considerable progress has been made in this direction by the study of homologous series of ethereal salts and alkyloxides, it can scarcely be claimed that any generalisations of wide application have yet been established. This is no doubt to be explained partly by the uncertainty attaching to the conventional method of expressing optical rotatory power, and partly by the fact that with few exceptions the compounds chosen for examination have been of too complex a character to admit of great emphasis being laid on the conclusions drawn from them. Owing chiefly to

the difficulty in preparing them, we are acquainted with but few structurally simple substances which could be utilised in such work. The ideal substance from this point of view would be an easily accessible compound, of low molecular weight, having only one asymmetric carbon atom, and containing no cyclic grouping; it would be an additional advantage if it contained a chemically reactive group or radicle directly attached to the asymmetric carbon atom, through the agency of which the effect of substitution, addition, or of the introduction of double linkings could be studied. The value of a substance containing a single asymmetric carbon atom in connexion with the application of Guye's modified equation has been pointed out by Bose (*Physikal. Zeitsch.*, 1908, **9**, 860).

The series of aldehydes of the type $\text{CHRR}'\cdot\text{CHO}$ fulfils the foregoing conditions, and since they are easily obtained by the general method of Darzens (*Compt. rend.*, 1904, **139**, 1214), it appeared to be of interest to ascertain whether these presumably racemic substances are capable of resolution into optical antipodes, or whether by other processes they could be obtained in active forms. The direct resolution of racemic aldehydes has been accomplished by Neuberg and Federer (*Ber.*, 1905, **38**, 868), who employed *d*-phenylamylhydrazine, a substance not easy to prepare in the pure state, and which, like most amyl compounds, might be expected to form oily derivatives. In a previous communication (*Trans.*, 1907, **91**, 1890) I have described the preparation of an optically active amine, namely, 4-bromo-3-aminophenyl- α -camphoramic acid, which it was hoped might be applied to the same purpose. The action of this base on hydratropaldehyde, $\text{CHMePh}\cdot\text{CHO}$, has now been examined, but the results obtained did not seem to warrant the extension of its use.

Attention has been drawn (*loc. cit.*) to the difficulty with which camphoric anhydride unites with the nitroanilines to form the nitrophenyl- α -camphoramic acids. This combination has now been effected in the case of *m*-nitroaniline. The nitro-acid obtained has been reduced to the amino-compound, and the behaviour of the product towards a racemic aldehyde studied. For this purpose butylchloral, $\text{CCl}_2\text{Me}\cdot\text{CHCl}\cdot\text{CHO}$, was selected, since Wheeler (*J. Amer. Chem. Soc.*, 1908, **30**, 136) has found that chloral readily condenses with primary aromatic amines, forming well-defined compounds. In the present instance, however, although condensation between one molecule of the aldehyde and two molecules of the base presented no difficulty, it was not found possible to resolve the product by fractional crystallisation into its optically active components.

A more promising method that suggests itself would be to resolve

a $\beta\beta$ -substituted glycidic acid by the aid of an alkaloid, and then to decompose the active salts by a mineral acid, when carbon dioxide is eliminated and the aldehyde produced. Experiments have been carried out in this direction, but although a sodium salt of β -phenyl- β -methylglycidic acid has been obtained having $[\alpha]_D + 16.6^\circ$ in aqueous solution, yet the corresponding aldehyde appears to be optically inactive. This, however, may be due to the fact that the acid itself contains two asymmetric carbon atoms, and it is possible that resolution has only been effected in the case of the carbon atom which ceases to be asymmetric on conversion of the acid into the aldehyde:



In the expectation of obtaining optically active bases by the reduction of nitro-derivatives of benzylidenecamphor, I have examined the action of *o*-, *m*-, and *p*-nitrobenzaldehyde on sodium camphor. Although this line of inquiry has been abandoned on account of the very poor yields obtained, the results of the experiments are recorded in the sequel.

A point of some interest has been noticed in connexion with the optical properties of the derivatives of α -camphoramic acid. It has usually been found that the rotatory power of a cyclic compound is considerably greater than that of the corresponding open-chain derivative. Thus the rotatory powers of esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyladipic acid (Haller, *Compt. rend.*, 1905, **140**, 1205). The hexahydrophthalic acids have much lower specific rotations than their anhydrides (Werner, *Ber.*, 1899, **32**, 3046). Many other instances might be quoted. Camphoric acid and its anhydride, however, form an exception to the rule, the acid having $[\alpha]_D + 46^\circ$ in alcohol, whilst the anhydride has $[\alpha]_D - 7.7^\circ$. Similarly, α -camphoramic acid has $[\alpha]_D + 45^\circ$ in acetone, whilst camphorimide has $[\alpha]_D - 10.1^\circ$. In order to ascertain whether this peculiarity was exhibited by the *N*-substituted amides and imides of camphoric acid, I have prepared several new members of this series, and determined their rotatory power in acetone solution at a temperature between 19° and 21° . Variations in the concentration of the solution between 1.5 and 3 parts per 100 have very little effect on the rotatory power.

The results are summarised on p. 408.

It will be noticed that the molecular rotatory power of the acid is always greater than that of its corresponding imide, except in the case of the α -naphthyl and *o*-bromophenyl derivatives. The difference between the molecular rotatory powers of the acid and

Derivative.	Camphoramic acid.		Camphorimide.	
	[α] _D .	[M] _D .	[α] _D .	[M] _D .
Methyl	33·24°	70·6°	7·26°	14·1°
Ethyl	17·1	38·8	8·87	18·5
<i>n</i> -Propyl	18·45	44·5	10·9	24·3
<i>n</i> -Butyl	15·8	40·3	12·8	30·3
<i>n</i> -Amyl	18·9	50·8	7·7	19·3
<i>n</i> -Hexyl.....	16·9	47·8	10·8	28·6
Allyl	13·54	32·4	7·95	17·6
<i>o</i> -Tolyl	33·9	98·0	15·7	43·0
<i>m</i> -Tolyl	31·0	89·0	17·6	47·0
<i>p</i> -Tolyl	37·0	107·0	12·7	34·0
α -Naphthyl ..	7·46	24·2	26·34	80·7
β -Naphthyl ..	64·9	210·9	18·0	55·2
4-Hydroxyphenyl	49·2	143·1	—	—
4-Ethoxyphenyl	39·5	130·0	18·5	55·0
2-Chlorophenyl	-16·4	-50·8	14·1	41·2
3-Chlorophenyl	37·0	114·0	16·2	47·0
4-Chlorophenyl	40·5	125·5	16·2	47·0
2-Bromophenyl	-11·8	-41·8	13·3	44·7
3-Bromophenyl	33·2	117·0	15·4	51·0
4-Bromophenyl	37·8	134·0	15·7	52·0
3-Nitrophenyl	32·0	102·4	1·7	5·1
3-Aminophenyl	39·9	116·5	—	—
4-Bromo-3-nitrophenyl ..	-48·4	-193·2 *	—	—
4-Bromo-3-aminophenyl ..	40·7	109·5 *	(feebly dextrorotatory)	—
4-Benzeneazophenyl	87·7	332·5 *	—	—

* In alcoholic solution.

imide in the case of *o*-, *m*-, and *p*-isomerides is always greatest in the *p*-compounds. The homologous series of alkyl derivatives show no marked regularity; it is noteworthy, however, that the two allyl compounds show distinctly lower rotatory power than the corresponding *n*-propyl derivatives, in this respect resembling the allylamides in the malic and tartaric series, which show abnormally low rotatory powers when compared with the propylamides (Frankland and Done, *Trans.*, 1906, **89**, 1861).

EXPERIMENTAL.

Attempted Preparation of Optically Active Hydratropaldehyde.

Hydratropaldehyde and 4-bromo-3-amino- α -camphoramic acid did not interact in alcoholic solution, either in the cold or on warming, and attempts to obtain a condensation product with benzaldehyde were equally unsuccessful.

Resolution of Sodium β -Phenyl- β -methylglycidate.

Preliminary experiments with the quinine salt of β -phenyl- β -methylglycidic acid having shown that this substance was unsuitable for the purpose, the brucine salt was prepared by adding

brucine hydrochloride (1 mol.), dissolved in the minimum amount of warm water, to a warm aqueous solution of sodium β -phenyl- β -methylglycidate (2 mols.). On allowing the solution to evaporate spontaneously over potassium hydroxide in a vacuum, clusters of radiating, irregular prisms separated, which were crystallised repeatedly from absolute alcohol until optically constant, care being taken to avoid prolonged heating with the solvent:

0.2402 gave 10.4 c.c. N_2 at 23° and 760 mm. $N=4.89$.

$C_{33}H_{36}O_7N_2$ requires $N=4.89$ per cent.

0.6475, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha - 1.14^\circ$, whence $[\alpha]_D - 17.7^\circ$.

0.6800, in 20 c.c. absolute alcohol, gave, in a 2-dcm. tube, $\alpha - 0.60^\circ$, whence $[\alpha]_D - 8.82^\circ$.

When rapidly heated, the salt melts and decomposes at $141-142^\circ$. It decomposes on boiling with water or when heated a few degrees above its melting point, giving brucine and hydratropaldehyde. A good yield of the latter was obtained when the salt was slowly heated under diminished pressure; the product was collected in three separate fractions, but each of these proved to be optically inactive when examined in ethereal or alcoholic solution. The mother liquor remaining from the preparation of the salt was pale brown in colour, and when kept in a vacuum deposited a small quantity of the crystalline brucine salt, together with a resinous substance which appeared to contain hydratropaldehyde together with the free alkaloid. Dilution of the liquid with water caused a further precipitation of brucine. The hydratropaldehyde was found to be inactive.

Sodium d- β -Phenyl- β -methylglycidate, $\begin{array}{c} CH_3 \\ \diagup \\ C_6H_5 \end{array} > C < \begin{array}{c} CH \cdot CO_2Na \\ \diagdown \\ O \end{array}$, was obtained by grinding the foregoing brucine salt with water containing the calculated amount of sodium hydroxide. The alkaloid was removed by repeated extraction with chloroform, and the solution allowed to evaporate in a vacuum. The sodium salt was finally obtained in colourless leaflets after three crystallisations from dilute alcohol:

0.3002 gave 0.1097 Na_2SO_4 . $Na=11.88$.

$C_{10}H_9O_3Na$ requires $Na=12.10$ per cent.

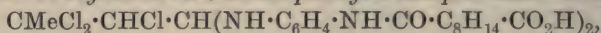
0.6000, in 20 c.c. water, gave, in a 2-dcm. tube, $\alpha + 1.00^\circ$, whence $[\alpha]_D + 16.6^\circ$.

When dissolved in water and treated with slightly less than the calculated amount of sulphuric acid, carbon dioxide was evolved, and the solution became turbid through the separation of hydratropaldehyde. In one experiment this was removed by steam dis-

tillation, and in another by extraction with ether; both specimens, however, appeared to be optically inactive when examined in 5 per cent. solutions of alcohol, chloroform, or ether. The aldehyde, moreover, gave a semicarbazone identical with that obtained from the racemic sodium salt.

Attempted Resolution of Butylchloral.—Condensation occurs readily when an aqueous solution of *m*-aminophenyl- α -camphoramic acid (see below) is shaken with butylchloral. It is advisable, however, to add the butylchloral (1 mol.) to a solution of the sodium salt of the acid (2 mols.). The aldehyde dissolves immediately with considerable development of heat.

Trichlorobutylidenebis-3-aminophenyl- α -camphoramic Acid,



separates as a bulky mass of colourless needles when the solution of its sodium salt is acidified with acetic acid. After crystallisation from dilute alcohol, it melts and decomposes at 126–130° when heated moderately rapidly. Attempts to resolve it by fractional crystallisation from this solvent and also from acetone were not successful, successive fractions showing practically the same rotatory power. Prolonged heating with solvents brings about decomposition:

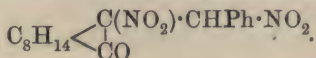
0.9081 gave 0.0510 AgCl. Cl = 13.89.

$\text{C}_{36}\text{H}_{47}\text{O}_6\text{N}_4\text{Cl}_3$ requires Cl = 14.38 per cent.

0.5110, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.40^\circ$, whence $[\alpha]_D + 27.4^\circ$.

Nitro-derivatives of Benzylidenecamphor.

The only nitro-derivative of benzylidenecamphor hitherto known has been described by Haller (*Compt. rend.*, 1895, **121**, 36). By the action of fuming nitric acid on benzylidenecamphor, a colourless compound was obtained, to which he ascribed the constitution:



The nitro-groups do not appear to be attached to the benzene nucleus, since the substance furnishes benzylidenecamphor on reduction.

Action of p-Nitrobenzaldehyde on Sodium Camphor.—The sodium camphor required in these experiments was prepared by the action of sodium or finely divided sodamide on camphor dissolved in dry ether, benzene, or toluene. The reactions appeared to follow the same course whichever method was adopted, the use of sodamide with ether, however, was preferred as giving cleaner products and

a better yield. On adding two-thirds of the calculated quantity of *p*-nitrobenzaldehyde to a well-cooled suspension of sodium camphor, a vigorous action ensued, accompanied by development of heat. The mixture was kept below 5° for an hour, and then heated for a short time on the water-bath. The reddish-brown, pasty mass was extracted with water, the layer of organic solvent separated, dried, and finally heated on the water-bath until the solvent and the greater part of unaltered camphor had been removed. The aqueous extract on the addition of an acid gave a voluminous yellow precipitate consisting chiefly of *p*-nitrobenzoic acid. The residue left after evaporation of the organic solvent appeared as a viscous, red oil, which slowly deposited yellow crystals. The oily matter was removed by extraction with cold alcohol and examined separately. The crystalline residue contained the following two substances.

I. A compound, $C_{34}H_{38}O_4N_2$.—This product is sparingly soluble in alcohol, ether, or benzene, and readily so in pyridine or carbon tetrachloride, from which it separates in small, orange-red prisms, melting at 280 — 281° . The compound is distinguished by its remarkably high rotatory power; it does not give Liebermann's reaction, and develops no coloration with alcoholic potash. Two determinations of the molecular weight in chloroform solution by the ebullioscopic method gave 422 and 446 respectively, the above formula requiring 538:

0.0913 gave 0.2529 CO_2 and 0.0597 H_2O . $C=75.52$; $H=7.25$.

0.3559 „ 12.8 c.c. N_2 at 18° and 744 mm. $N=5.65$.

$C_{34}H_{38}O_4N_2$ requires $C=75.82$; $H=7.06$; $N=5.20$ per cent.

0.0939, in 25 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 4.55^{\circ}$, whence $[\alpha]_D + 605^{\circ}$, and $[M]_D + 3255^{\circ}$.

II.—4-Nitrobenzylidenecamphor, $C_8H_{14} \begin{smallmatrix} \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2 \\ | \\ \text{CO} \end{smallmatrix}$.—This

compound separates from alcohol in bright yellow, glistening leaflets, melting at 156 — 157° ; it is sparingly soluble in alcoholic potassium hydroxide, giving a yellow solution. Concentrated sulphuric acid develops an orange-red coloration:

0.1012 gave 0.3148 CO_2 and 0.0592 H_2O . $C=71.71$; $H=6.38$.

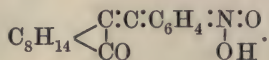
0.1780 „ 7.6 c.c. N_2 at 16° and 754 mm. $N=4.82$.

$C_{17}H_{19}O_3N$ requires $C=71.59$; $H=6.66$; $N=4.88$ per cent.

0.3102, in 20 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 3.55^{\circ}$, whence $[\alpha]_D + 437^{\circ}$, and $[M]_D + 1345^{\circ}$.

Examination of the Alcoholic Extract.—A deep red oil, having a slight odour of camphor, remained after removal of the alcohol by evaporation. The oil is insoluble in water, but freely soluble in the usual organic media; on adding alkali hydroxide to its alcoholic solution, an intense purple coloration is developed, which, on

dilution with water, changes to red. The colour is destroyed by acids, but restored by alkalis. It is possible that this product contains an enolic form of 4-nitrobenzylidenecamphor:



A chromophoric oil having similar properties has been described by Forster, who obtained it by the action of *p*-nitrobenzyl chloride on isonitrosocamphor in presence of sodium ethoxide (Trans., 1908, **93**, 249). Decomposition occurs when the oil is distilled under diminished pressure, and all attempts to isolate a pure compound or prepare a crystalline derivative have failed.

No chromophoric substance is formed if the temperature of reaction is allowed to rise during the preparation; under these conditions, the main product is the compound $\text{C}_{34}\text{H}_{38}\text{O}_4\text{N}_2$, together with a very insoluble brown substance which has not yet been obtained in a state of purity. To ascertain whether the presence of the camphor nucleus is essential for its formation, experiments have been carried out on the action of *p*-nitrobenzaldehyde on the sodium derivatives of ethyl acetoacetate, carvone, and pulegone; no chromophoric product was recognised, however, and this would appear to exclude the possibility of the colour having arisen from the action of the alkali on any derivative of dinitrostilbene. It may be mentioned that the sodium derivative of pulegone is very readily prepared by the action of sodamide on an ethereal solution of pulegone. The action proceeds briskly without warming, and a good yield is obtained.

Action of o- and m-Nitrobenzaldehyde on Sodium Camphor.

2-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$, prepared in the same way as the 4-nitro-compound, occurs as well-formed, light brown prisms, melting at 116–117°. A solution in chloroform gave $[\alpha]_D +50^\circ$ approximately; owing to the absorption of light, the rotatory power could not be accurately determined. The compound itself gives no coloration with alcoholic potassium hydroxide, but the oily material from which it is separated develops an intense purple coloration with this reagent:

0.2633 gave 11.9 c.c. N_2 at 28° and 766 mm. $\text{N}=4.99$.

$\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{N}=4.88$ per cent.

3-Nitrobenzylidenecamphor, $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$.—This compound and *m*-nitrobenzoic acid are the only products of the action of *m*-nitrobenzaldehyde on sodium camphor. It was obtained as a yellow oil, which, on addition of alcohol, rapidly solidified. When

crystallised from hot alcohol, it forms very pale yellow needles, melting at 110—111°:

0.2024 gave 9.4 c.c. N_2 at 19° and 748 mm. $N=5.13$.

$C_{17}H_{19}O_3N$ requires $N=4.88$ per cent.

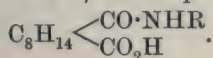
0.0934, in 15 c.c. chloroform, gave, in a 2-dcm. tube, $\alpha_D + 3.92^\circ$, whence $[\alpha]_D + 311^\circ$, and $[M]_D + 783^\circ$.

Alkyl Derivatives of α -Camphoramic Acid, $CO_2H \cdot C_8H_{14} \cdot CO \cdot NHR$.

The following new members of the series were prepared by the interaction of camphoric anhydride (1 mol.) with an alcoholic solution of the amine (2 mols.). After purification by conversion into the sodium salt, the free acid was regenerated by the addition of hydrochloric acid and crystallised from dilute acetone:

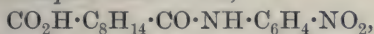
Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
Ethyl	$C_{12}H_{21}O_3N$	Hexagonal leaflets	173—175°	$N=6.08$	6.17
<i>n</i> -Propyl... ..	$C_{13}H_{23}O_3N$	Hexagonal leaflets	187—188	$N=5.79$	5.81
<i>n</i> -Butyl	$C_{14}H_{25}O_3N$	Hexagonal leaflets	124—125	$C=65.71$ $H=9.48$	65.89 9.80
<i>n</i> -Amyl	$C_{15}H_{27}O_3N$	Crystalline mass	—	$C=66.58$ $H=10.25$	66.91 10.03
<i>n</i> -Hexyl	$C_{16}H_{29}O_3N$	Hexagonal leaflets	123—124	$N=5.21$	4.95
Allyl	$C_{13}H_{21}O_3N$	Leaflets	157—158	$N=5.66$	5.87

Aryl Derivatives of α -Camphoramic Acid,



In most cases these compounds are readily obtained by heating an intimate mixture of camphoric anhydride and the substituted amine for a few minutes at 150—180°. In the case of *m*-nitroaniline, α -naphthylamine, and ortho-substituted amines, it is necessary to heat for a longer period in sealed tubes.

3-Nitrophenyl- α -camphoramic Acid,



is prepared by heating 13 grams of camphoric anhydride with 10 grams of *m*-nitroaniline at 150° for one hour in a sealed tube. The crystalline mass is dissolved in dilute ammonia, the solution filtered after twenty-four hours, and then acidified. The first few drops of acid precipitate a brown, resinous product, but further addition of acid yields the required compound in a state of purity. It is crystallised from acetic acid containing a little stannous chloride, and finally from alcohol, from which it separates in large,

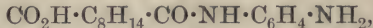
colourless, hexagonal leaflets, which darken at about 200° , and melt and decompose at $212-213^{\circ}$:

0.3052 gave 18.6 c.c. N_2 at 20° and 754 mm. $N=8.71$.

$C_{16}H_{20}O_5N_2$ requires $N=8.75$ per cent.

0.6178, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.97^{\circ}$, whence $[\alpha] + 32.0^{\circ}$.

3-Aminophenyl- α -camphoramic Acid,



prepared from the foregoing compound by reduction with ferrous sulphate in ammoniacal solution, forms small, colourless needles, melting at $196-197^{\circ}$:

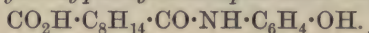
0.2000 gave 16.6 c.c. N_2 at 21° and 766 mm. $N=9.53$.

$C_{16}H_{22}O_3N$ requires $N=9.65$ per cent.

0.3908, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.56^{\circ}$, whence $[\alpha]_D + 39.9^{\circ}$.

The *acetyl* derivative crystallises in silky needles, melting at $220-221^{\circ}$. The *hydrochloride* of the base is easily soluble in water, and on diazotisation yields a clear solution which, on the addition of alkaline β -naphthol, furnishes a bright red azo-compound. A solution of the base in dilute alcohol gives an immediate precipitate on the addition of an aldehyde; this arises from condensation of two molecules of the base with one of the aldehyde.

4-Hydroxyphenyl- α -camphoramic Acid,



A brisk reaction occurs when camphoric anhydride and *p*-aminophenol are heated together. The dark-coloured product contains small quantities of a substance characterised by the intense purple coloration developed with aqueous alkali hydroxides; it was crystallised from alcohol until the mother liquor no longer showed this reaction. Recrystallisation from acetic acid, after treatment with animal charcoal, gave small, pale brown prisms. The melting point was somewhat indefinite, the compound sintering at 236° and decomposing at 250° . The product after fusion dissolved in aqueous alkalis, giving deep purple solutions, probably owing to the formation of a phthalein:

0.0986 gave 0.2385 CO_2 and 0.0648 H_2O . $C=65.80$; $H=7.30$.

$C_{16}H_{21}O_4N$ requires $C=65.98$; $H=7.22$ per cent.

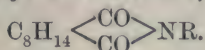
0.3641, in 20 c.c. acetone, gave, in a 2-dcm. tube, $\alpha_D + 1.80^{\circ}$, whence $[\alpha]_D + 49.16^{\circ}$.

The following aryl derivatives of α -camphoramic acid were also prepared:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
<i>o</i> -Tolyl.....	C ₁₇ H ₂₃ O ₃ N	Long needles	194—196°	N=4·72	4·84
<i>m</i> -Tolyl	C ₁₇ H ₂₃ O ₃ N	Needles	208—209	N=4·76	4·84
<i>p</i> -Tolyl *	C ₁₇ H ₂₃ O ₃ N	Leaflets	212—214	N=4·96	4·84
α -Naphthyl.....	C ₂₀ H ₂₅ O ₃ N	Needles	233—235	N=4·31	4·31
β -Naphthyl.....	C ₂₀ H ₂₅ O ₃ N	Lustrous leaflets	210—212	N=4·68	4·31
4-Ethoxyphenyl...	C ₁₈ H ₂₅ O ₄ N	Long needles	195—197	N=4·35	4·39
2-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCl	Minute crystals	139—140	Cl=11·22	11·47
3-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCl	Leaflets	207—209	Cl=11·35	11·47
4-Chlorophenyl ...	C ₁₆ H ₂₀ O ₃ NCl	Prisms	192—194	Cl=11·38	11·47
2-Bromophenyl ...	C ₁₆ H ₂₀ O ₃ NBr	Vitreous mass	about 78	Br=22·42	22·60
3-Bromophenyl ...	C ₁₆ H ₂₀ O ₃ NBr	Small tablets	215—217	Br=22·54	22·60

* This compound, together with the corresponding imide, has recently been described by Abati and Notaris (*Gazzetta*, 1909, **39**, ii, 219). These authors give the melting point 201—209° for the acid and 131° for the imide.

N-Alkyl and Aryl Derivatives of Camphorimide,



By boiling a solution of a *N*-substituted α -camphoramic acid in glacial acetic acid with acetyl chloride for two hours, and pouring the liquid into excess of dilute ammonia, the corresponding imide is obtained in almost theoretical yield. The following were prepared:

Derivative.	Empirical formula.	Crystalline form.	M. p.	Analysis.	
				Found.	Theory, per cent.
<i>n</i> -Propyl	C ₁₃ H ₂₁ O ₂ N	Prisms	40—41°	C=69·92	69·95
<i>n</i> -Butyl	C ₁₄ H ₂₃ O ₂ N	Lath-like crystals	61—62	H=9·37	9·42
<i>n</i> -Amyl	C ₁₅ H ₂₅ O ₂ N	Oil	—	N=6·13	5·91
<i>n</i> -Hexyl	C ₁₆ H ₂₇ O ₂ N	Oil	—	N=5·50	5·58
<i>o</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Long needles	195—196	N=6·31	5·28
<i>m</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Glistening leaflets	117—118	N=5·21	5·16
<i>p</i> -Tolyl	C ₁₇ H ₂₁ O ₂ N	Flat prisms	127—128	N=5·27	5·16
α -Naphthyl.....	C ₂₀ H ₂₁ O ₂ N	Stout prisms	211—212	C=74·98	75·26
β -Naphthyl.....	C ₂₀ H ₂₁ O ₂ N	Small needles	167—168	H=7·61	7·75
2-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCl	Flat prisms	125—126	N=4·68	4·56
3-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCl	Needles	172—173	N=4·57	4·56
4-Chlorophenyl ...	C ₁₆ H ₁₈ O ₂ NCl	Prisms	162—163	Cl=11·97	12·18
2-Bromophenyl ...	C ₁₆ H ₁₈ O ₂ NBr	Small prisms	139—140	Cl=12·03	12·18
3-Bromophenyl ...	C ₁₆ H ₁₈ O ₂ NBr	Needles	184—185	N=4·89	4·80
8-Nitrophenyl.....	C ₁₆ H ₁₈ O ₄ N ₂	Rhombic prisms	146—147	Br=23·57	23·80
				Br=23·68	23·80
				N=8·97	9·27

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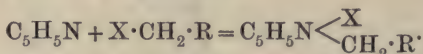
XLVI.—*The Relation between Reactivity and Chemical Constitution of Certain Halogen Compounds.*

By HANS THACHER CLARKE.

THE reactivity of the halogens in organic halogen compounds has been studied by various investigators: Wislicenus (*Annalen*, 1882, **212**, 239), with ethyl sodioacetoacetate; Hecht, Conrad, and Brückner (*Zeitsch. physikal. Chem.*, 1889, **4**, 273), with sodium ethoxide; Menshutkin (*Zeitsch. physikal. Chem.*, 1890, **5**, 589), with triethylamine; Burke and Donnan (*Trans.*, 1904, **85**, 555; *Zeitsch. physikal. Chem.*, 1909, **69**, 148), with silver nitrate; Slator (*Trans.*, 1904, **85**, 1286; 1905, **87**, 482), Slator and Twiss (*Trans.*, 1909, **95**, 93), with sodium thiosulphate; Senter (*Trans.*, 1907, **91**, 460; 1909, **95**, 1827), with water and with alkalis; but no definite conclusions appear to have been drawn as to the relations between reactivity and constitution.

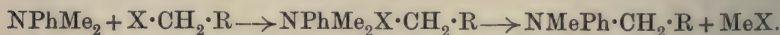
The present paper deals with compounds of the type $X \cdot CH_2 \cdot R$, the object being to study the influence of the nature of the group (R) on the reactivity of the halogen (X).

The reactivity was determined by the measurement of the velocity of the reaction between pyridine and the halogen compound in absolute alcoholic solution, identical conditions being observed throughout the series of experiments:



From the scheme representing the reaction, it is evident that ionic reactions are improbable.

Attempts were at first made with ethylaniline and dimethylaniline at the temperature of boiling alcohol, but it was found that the values of "K," calculated for a bimolecular reaction, decreased with the progress of the reaction, this effect being doubtless due to "heterospasis":



Pyridine was accordingly selected as a tertiary base in which no such decomposition could occur. Moreover, as pyridine is more strongly basic than the above-mentioned derivatives of aniline, the reaction could take place with measurable velocity at a lower temperature.

Equal volumes of *N*/2-solutions of pyridine and the halogen compound were mixed and maintained at the temperature of 55.6°, afforded by a water-bath surrounded with boiling acetone

under constant pressure, aliquot portions being withdrawn at intervals and the ionised halogen titrated with silver nitrate. The constant was calculated from the usual formula for a bimolecular reaction, namely:

$$K = \frac{1}{C_0 \cdot t} \cdot \frac{C_t}{C_0 - C_t}$$

In nearly every case the values of K did not vary from those required for a bimolecular reaction by more than experimental error.

The experimental results are set forth in the following table; they will be discussed in detail on subsequent pages:

	X.	R.	K.
<i>n</i> -Propyl bromide	Br·CH ₂ ·	Et	0·0179
Allyl ,,	Br·CH ₂ ·	CH:CH ₂	1·253
Benzyl ,,	Br·CH ₂ ·	Ph	5·118
Cinnamyl ,,	Br·CH ₂ ·	CH:CH·Ph	0·472
Bromoacetic acid	Br·CH ₂ ·	CO ₂ H	0·666
Methyl bromoacetate	Br·CH ₂ ·	CO ₂ Me	0·919
Ethyl ,,	Br·CH ₂ ·	CO ₂ Et	1·004
<i>n</i> -Propyl ,,	Br·CH ₂ ·	CO ₂ Pr ^a	0·752
<i>iso</i> Propyl ,,	Br·CH ₂ ·	CO ₂ Pr ^b	1·048
<i>n</i> -Butyl ,,	Br·CH ₂ ·	CO ₂ ·CH ₂ ·CH ₂ Et	0·770
<i>tert.</i> -Butyl ,,	Br·CH ₂ ·	CO ₂ ·CMe ₃	0·934
Phenyl ,,	Br·CH ₂ ·	CO ₂ Ph	1·927
Benzyl ,,	Br·CH ₂ ·	CO ₂ ·CH ₂ Ph	1·211
Allyl ,,	Br·CH ₂ ·	CO ₂ ·C ₃ H ₅	0·768
Ethyl β-bromopropionate	Br·CH ₂ ·	CH ₂ ·CO ₂ Et	0·0277
Bromoacetal	Br·CH ₂ ·	CH(OEt) ₂	0·012
Chloroacetamide	Cl·CH ₂ ·	CO·NH ₂	0·01115
Chloroacetanilide	Cl·CH ₂ ·	CO·NHPh	0·0264
Bromoacetanilide	Br·CH ₂ ·	CO·NHPh	1·533
Diphenylchloroacetamide	Cl·CH ₂ ·	CO·NPh ₂	0·0341
Chloroacetone	Cl·CH ₂ ·	CO·Me	0·0686
Chloroacetophenone	Cl·CH ₂ ·	CO·Ph	0·1339
Bromoacetophenone	Br·CH ₂ ·	CO·Ph	7·269

The first fact established was that in a compound of the type X·CH₂·R the reactivity of the halogen, as determined by the above method, was controlled by the residual affinity of the atom or group (R) directly attached to the methylene carbon atom. The following series will illustrate this conclusion:

	K.
<i>n</i> -Propyl bromide	0·0179
Methyl bromoacetate	0·919
Allyl bromide	1·253
Benzyl ,,	5·118

Monochloromethyl ether and bromonitromethane were also examined. In both these cases there are present groups to which a large amount of residual affinity is attributable (OMe; NO₂). Chloromethyl ether reacted so rapidly with alcoholic pyridine that no measurement could be obtained; whereas bromo-

nitromethane formed a pyridine salt at once, and very little elimination of bromine ensued.

Taking, then, this rule as a basis, an attempt has been made to determine the degree of unsaturation in various compounds of this type in order to elucidate the nature of the different groups involved.

The effect of conjugation of a phenyl nucleus with an ethenoid linking appears to diminish the total residual affinity inherent in the carbon atom in the α -position with respect to the methylene group, the reactivity of cinnamyl bromide being less than one-half of that of allyl bromide:

Cinnamyl bromide	$\text{Ph}\cdot\text{CH}:\text{CH}\cdot\text{CH}_2\text{Br}$	$K=0\cdot472$
Allyl ,,	$\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\text{Br}$	$K=1\cdot253$

Turning now to the derivatives of chloro- and bromo-acetic acids, it was found that the reactivity of the halogen varied with the nature of the radicle to which the halogen-acyl group was attached.

When equimolecular quantities of pyridine and bromoacetic acid were mixed in alcoholic solution, it was found, contrary to expectation, that elimination of bromine took place along the lines of a bimolecular reaction. This fact would tend to point to the absence of stable salt-formation in absolute alcohol:

Bromoacetic acid	$K=0\cdot666$
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The reactivity of the halogen in the following series of saturated aliphatic esters was examined:

	K .		K .
Methyl bromoacetate	0·919	<i>iso</i> Propyl bromoacetate	1·048
Ethyl ,,	1·004	<i>n</i> -Butyl ,,	0·770
<i>n</i> -Propyl ,,	0·752	<i>tert.</i> -Butyl ,,	0·934

The phenyl, benzyl, and allyl esters of bromoacetic acid were examined in the same manner:

	K .
Phenyl bromoacetate	1·927
Benzyl ,,	1·211
Allyl ,,	0·768

In phenyl bromoacetate, which exhibits a greatly exalted reactivity, the alcoholic radicle contains the greatest residual affinity. In benzyl bromoacetate, in which a methylene group is interposed between the phenyl and the bromoacetoxyl groups, the effect still persists, although considerably diminished. The reactivity of the allyl ester, when compared with that of the *n*-propyl ester, shows a slight exaltation—to a less extent, however, owing to the less powerful influence of the ethenoid as compared with the benzenoid grouping.

Since the values obtained from allyl bromoacetate and benzyl

bromoacetate indicate that the influence of the unsaturated group is appreciable even when situated in the β -position, the reactivity of ethyl β -bromopropionate was measured:

Ethyl β -bromopropionate $K=0.0277$

This value, when compared with the saturated standard, *n*-propyl bromide ($K=0.0179$), is sensibly exalted. Bromoacetal, on the other hand, yields a value ($K=0.012$) which shows the reactivity of the halogen to be slightly depressed.

In the series of halogen-acetylammides, the reactivity of the halogen compounds was measured:

	<i>K.</i>		<i>K.</i>
Chloroacetamide	0.01115	Bromoacetanilide	1.533
Chloroacetanilide	0.0264	Diphenylchloroacetamide..	0.0341

In the case of the halogen-acetanilides, the reactivity constant of the bromine derivative is 58.1 times as great as that of the chlorine derivative. Taking this ratio, the value calculated from chloroacetamide yields $K=0.648$ for bromoacetamide, a substance difficult to obtain in a high state of purity, and, moreover, insufficiently soluble in alcohol.

The same rule thus holds good for the $\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O}\cdot$ and the $\text{Br}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}\cdot$ structures, the replacement of hydrogen by phenyl giving rise to increased reactivity of the halogen, as the following table shows:

	<i>K.</i>		<i>K.</i>
Bromoacetic acid.....	0.666	(Bromoacetamide	0.648)
Phenyl bromoacetate	1.927	Bromoacetanilide	1.533

The reactivities of halogenated ketones were found to be greatly in excess of those of the corresponding carboxylic compounds enumerated above:

	<i>K.</i>
Chloroacetone	0.0686
Chloroacetophenone	0.1339
Bromoacetophenone	1.269

from which the constant for bromoacetone can be calculated, being approximately $K=3.720$. In the case of the ketones, as in the case of bromoacetic esters, the replacement of a methyl group by a phenyl group occasions approximately doubled reactivity.

Two series of measurements were carried out in an aqueous-alcoholic solution (25 c.c. absolute alcohol diluted to 100 c.c. with water), the substances examined being methyl bromoacetate and potassium bromoacetate, and the initial concentration of the reacting substances $N/4$ before mixing:

	<i>K.</i>
Methyl bromoacetate	14.61
Potassium „	9.07

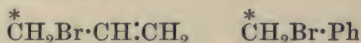
It will be observed that a far greater velocity of reaction ensued in the presence of water than in absolute alcohol. The ratio between the constants obtained for these substances in aqueous-alcoholic solution is of the same order as that between those obtained for methyl bromoacetate and for bromoacetic acid in alcoholic solution:

Methyl bromoacetate	(0.919) : bromoacetic acid	(0.666) = 1 : 0.775
„ „	(14.61) : potassium bromoacetate	(9.07) = 1 : 0.621

It would thus appear that no radical change in constitution occurs during salt-formation and esterification.

Discussion of Results.

The author inclines to regard the variation of the reactivity of the halogen in compounds containing unsaturated groups in the β -position as due to the weakening of the bonds attached to the α -carbon atom caused by the strengthening of the bond between the unsaturated group and the α -carbon atom. To take the case of allyl bromide and benzyl bromide, all residual affinity of the methylene carbon atom (*):



is absorbed by the unsaturated group, leaving the remaining three atoms less strongly attached to the carbon atom. This is borne out by the observation of Wislicenus (*loc. cit.*) that the halogen in vinyl iodide ($\text{CH}_2\cdot\text{CH}\cdot$) is subnormally reactive. The subnormal reactivity of the halogens in aryl halides may perhaps be due to the same cause. This view of the variable strength of affinities with varying substituents has already been put forward by Claus (*Ber.*, 1881, **14**, 432), and fully discussed by Werner and by Flürscheim.

Of the compounds containing the halogen-acetyl grouping, the greatest reactivity of the halogen is to be found among the ketones. This tends to show that the ketonic carbonyl group possesses more residual affinity than the carboxylic and carbamidic carbonyl group. It has long been suspected that in the carboxyl group the two oxygen atoms exert some mutual attraction, and in a recent publication Miss Smedley (*Trans.*, 1909, **95**, 231) has assigned to the carboxyl group a constitution, $\cdot\text{C}\begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$, in which the third and fourth valencies of the two oxygen atoms are united.

Now, it was shown above that in the case of phenyl bromoacetate the reactivity of the halogen is approximately double that of the corresponding methyl ester, and this fact indicates that some influence must be at work which transmits the effect through a series of atoms so as to exalt the reactivity of the halogen.

Hitherto all formulation of the carboxyl group has been essentially of a static nature. The old formula, $\cdot\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O}\cdot \end{smallmatrix}$, must be discarded, since it furnishes no distinction between the carboxylic and ketonic carbonyl groups, and the formula advocated by Goldschmidt (*Zeitsch. Elektrochem.*, 1904, **10**, 221), $\cdot\text{C}:\text{O}:\text{O}\cdot$, is difficult to reconcile with the chemical and physical properties of the group.

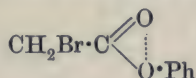
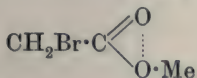
Miss Smedley's view of the constitution of the carboxyl group is in harmony with the results above mentioned, except in so far that its static nature gives no explanation of the variations in reactivity due to differences in the alcoholic radicle. The author therefore suggests that this formulation should be modified in such a way that the greater or less unsaturated character of the carbonyl group is expressed.

There are two possible methods of regarding the problem. The first is that the bond between the oxygen atoms is variable in intensity, resulting in a formula of this nature: $\cdot\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O}- \end{smallmatrix}$; the

second being that while the attraction between the oxygen atoms remains constant, the bond between the hydroxylic oxygen atom and the carbon atom varies in intensity, requiring a formula of the

type $\cdot\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{O} \\ \parallel \text{O} \end{smallmatrix}$. Considering the problem as a whole, the evidence tends to favour the first view.

A comparison of the conditions obtaining in methyl bromoacetate and phenyl bromoacetate may serve to illustrate this interpretation:



In the phenyl ester a greater proportion of the residual affinity of the hydroxylic oxygen atom is absorbed by the phenyl group than in the case of the methyl ester, so that the attraction between the oxygen atoms is lessened. A more unsaturated or, it might be said, a more ketonic form of carbonyl is thus produced, with consequent increase of reactivity of the bromine atom.

A similar structure may be applied to the amides: $\cdot\text{C}\begin{smallmatrix} \nearrow \text{O} \\ \searrow \text{N}\cdot \end{smallmatrix}$.

Replacement of the amidic hydrogen atoms by groups rich in residual affinity, such as phenyl, enhances the ketonic character of the carbonyl group.

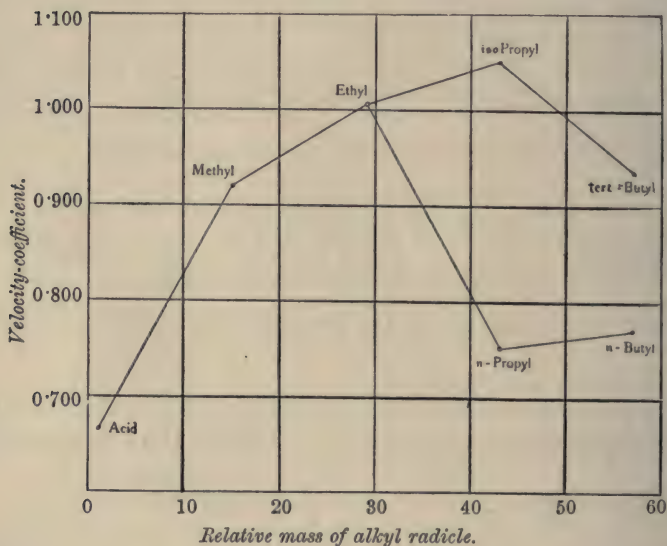
The variations observed through the series of aliphatic esters

which were examined are interesting, and point to differences in residual affinity of the several alkyl groups.

The free acid is less reactive than any of the esters, whilst the reactivity increases from the methyl ester through the ethyl ester to the *isopropyl* ester, that is, on successive substitution of the hydrogen atoms of the methyl group. Slator (*Trans.*, 1905, **87**, 481) also has found that ethyl bromoacetate is more reactive towards sodium thiosulphate than methyl bromoacetate. The reactivity of the tertiary butyl ester, however, falls to a value approximating that of the methyl ester.

On continuing substitution in a normal chain, the reactivity of

FIG. 1.



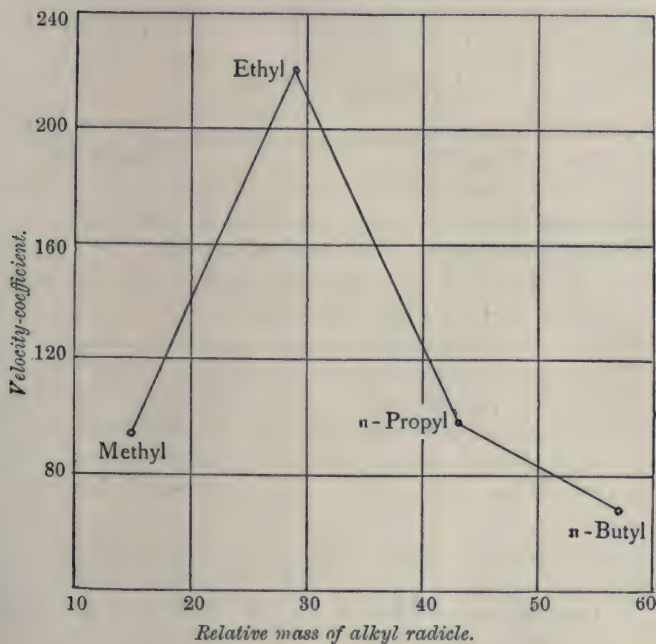
the *n*-propyl ester falls to a strikingly low value, rising again slightly in the case of the *n*-butyl ester. Thus, both the butyl esters examined display anomalous reactivity, breaking the continuity of the curves. The curve furnished by the normal esters, however, perhaps displays the periodic rise and fall observed in many of the physical properties of homologous series.

It may here be mentioned that these results are strictly comparable, as steric considerations can play no part in the elimination of bromine from bromoacetic esters.

The results found by Burke and Donnan (*loc. cit.*) for the reactivities of the alkyl iodides produce a curve, which, while similar in appearance, leads to the opposite conclusion. The

author's results tend to show that the residual affinity of the normal series of alkyl groups rises from methyl to ethyl, and falls to *n*-propyl, rising again slightly to *n*-butyl. On the other hand, since the halides of groups rich in residual affinity, such as phenyl or vinyl, have been shown to be distinctly sluggish towards halogen eliminating agents, it would follow from the work of Burke and Donnan that the residual affinity would be at a minimum in the ethyl radicle, increasing towards methyl on the one hand, and towards *n*-propyl and *n*-butyl on the other. A satisfactory explanation remains yet to be put forward to account for the discordant results

FIG. 2.



obtained for reaction velocity measurements in so far as the alkyl groups are concerned.

With regard to the variations in reactivity due to the structure of the alkyl radicles, no influence ascribable to "alkylene" or "alkylidene" dissociation (Nef, *Annalen*, 1899, **309**, 126) can be at work, dissociation of this type being highly improbable in carboxylic esters.

The measurements carried out with methyl bromoacetate indicate that the reaction with pyridine takes place with far greater velocity in aqueous alcohol than in absolute alcoholic solution. Slator and

Twiss (Trans., 1909, **95**, 99), on the other hand, find that sodium thiosulphate reacts more rapidly with methyl iodide and with chloroacetone in aqueous-alcoholic solution than in pure water.

In the halogen acetic acids and their derivatives, the influence between the halogen atom and the carboxyl group may be regarded as mutual, since Lichty (*Amer. Chem. J.*, 1895, **17**, 27) has shown that the initial velocities of esterification of chloro- and bromo-acetic acids by ethyl alcohol are greater than that of acetic acid. Lichty has also shown (*Annalen*, 1902, **319**, 369) that the initial esterification velocity and affinity constants of the α -halogen-fatty acids greatly exceed those of the β - and γ -halogen-fatty acids. This is in entire harmony with the decreased reactivity of the bromine in ethyl β -bromopropionate as compared with ethyl bromoacetate.

EXPERIMENTAL.

The substances employed for the reactivity measurements were in most cases purchased from Kahlbaum, or prepared by standard methods. Semi-normal solutions of pyridine and the various halogen compounds in absolute alcohol were prepared, 50 c.c. of each solution being mixed and maintained at 55.6°. At definite intervals of time, 10 c.c. were withdrawn and titrated with standard silver nitrate (approximately $N/10$), the pipettes being standardised for the temperature. In some cases, potassium chromate was used as an indicator, in others, Volhard's thiocyanate method was employed to determine the end-point. The 10 c.c. of solution were added to about 100 c.c. of cold distilled water, covered, when the substances were highly reactive, with a layer of ether to remove the unchanged halogen compounds from the action of the silver nitrate.

The following measurements were carried out in absolute alcoholic solution; temperature 55.6°; initial concentration $N/4$; t represents the time-interval in hours, C_t the percentage decomposition, and K the velocity-coefficient:

n-Propyl Bromide.

t	0.000	16.750	19.500	21.584	24.000
C_t	0.00	6.80	8.00	8.80	9.80
K	—	0.0174	0.0182	0.0179	0.0181

Mean value of $K=0.0179$.

Allyl Bromide.

t	0.000	1.000	1.333	2.333	2.500	3.000
C_t	0.00	23.80	29.58	42.50	43.79	48.80
K	—	1.248	1.258	1.268	1.246	1.245

Mean value of $K=1.253$.

Benzyl Bromide.

t	0.000	0.500	0.667	0.834	1.000	1.167
C_t	0.00	39.55	46.47	50.91	56.11	60.05
K	—	5.231	5.209	4.978	5.022	5.150

Mean value of $K=5.118$.

Cinnamyl Bromide.

t	0.000	0.167	0.767	1.917	3.250
C_t	0.00	1.97	8.27	18.51	27.59
K	—	0.482	0.471	0.475	0.469

Mean value of $K=0.472$.

Bromoacetic Acid.

t	0.000	0.684	1.033	1.333	1.500	1.667	1.833
C_t ...	0.00	9.00	14.60	18.40	20.00	21.60	24.00
K ...	—	0.642	0.662	0.676	0.667	0.660	0.688

Mean value of $K=0.666$.

Methyl Bromoacetate.

t	0.000	1.000	1.500	3.000	3.500	4.000	4.500
C_t ...	0.00	18.43	25.72	41.09	45.30	47.21	50.66
K ...	—	0.904	0.923	0.930	0.948	0.894	0.914

Mean value of $K=0.919$.

Ethyl Bromoacetate.

t ...	0.000	1.000	2.000	3.000	4.000	4.500	5.000	5.500	6.000
C_t ...	0.00	20.00	33.80	43.40	50.52	53.00	55.32	57.60	59.66
K ...	—	1.000	1.021	1.022	1.021	1.003	0.991	0.988	0.984

Mean value of $K=1.004$.

n-Propyl Bromoacetate.

t	0.000	1.500	2.500	3.584	4.500
C_t	0.00	22.07	31.91	40.40	45.60
K	—	0.755	0.750	0.757	0.744

Mean value of $K=0.752$.

isoPropyl Bromoacetate.

t	0.000	1.000	1.500	2.000	2.500	3.000
C_t ...	0.00	20.88	27.97	34.67	39.40	44.11
K ...	—	1.055	1.030	1.060	1.040	1.053

Mean value of $K=1.048$.

n-Butyl Bromoacetate.

t	0.000	1.333	2.000	2.500	3.000
C_t	0.00	20.09	28.36	32.30	36.62
K	—	0.754	0.792	0.764	0.771

Mean value of $K=0.770$.

tert.-Butyl Bromoacetate.

t	0.000	1.000	1.800	2.250	2.500
C_t	0.00	19.00	29.90	34.40	36.80
K	—	0.938	0.936	0.932	0.932

Mean value of $K=0.934$.*Phenyl Bromoacetate.*

t ...	0.000	0.433	0.600	0.767	0.934	1.100	1.267	1.433	1.600
C_t ...	0.00	17.28	22.28	27.28	31.11	34.95	37.67	41.70	43.40
K ...	—	1.929	1.911	1.958	1.936	1.963	1.907	1.915	1.919

Mean value of $K=1.927$.*Benzyl Bromoacetate.*

t	0.000	0.784	1.000	1.333	1.584	2.350	2.817	3.000
C_t	0.00	18.71	22.83	28.95	32.60	42.55	46.10	47.29
K	—	1.174	1.180	1.244	1.204	1.268	1.208	1.196

Mean value of $K=1.211$.*Allyl Bromoacetate.*

t	0.000	0.834	2.067	3.000	3.750
C_t	0.00	13.79	28.36	36.36	41.78
K	—	0.769	0.766	0.771	0.765

Mean value of $K=0.768$.*Ethyl β -Bromopropionate.*

t	0.000	5.250	21.500	24.000	27.500	29.500
C_t	0.00	3.94	12.20	13.50	15.35	16.78
K	—	0.0313	0.0258	0.0260	0.0264	0.0273

Mean value of $K=0.0277$.*Bromoacetal.*

t	0.000	18.000	21.000	26.000
C_t	0.00	5.21	6.02	6.87
K	—	0.0122	0.0122	0.0114

Mean value of $K=0.012$.*Chloroacetamide.*

t	0.000	19.170	21.167	23.500	45.333
C_t	0.00	5.09	5.76	6.14	11.22
K	—	0.01120	0.01155	0.01113	0.01070

Mean value of $K=0.01115$.*Chloroacetanilide.*

t	0.000	4.600	5.417	6.367	20.750	24.066
C_t	0.00	2.96	3.55	3.94	12.01	13.20
K	—	0.0265	0.0274	0.0258	0.0268	0.0253

Mean value of $K=0.0264$.

Bromoacetanilide.

t ...	0.000	1.000	1.500	1.934	2.834	3.283	3.483
C_t ...	0.00	27.65	36.50	41.85	52.80	56.35	57.50
K ...	—	1.463	1.532	1.485	1.578	1.573	1.565

Mean value of $K=1.533$.*Diphenylchloroacetamide.*

t	0.000	10.500	12.000	14.000	15.500	18.500
C_t	0.00	8.20	9.40	10.60	11.80	13.40
K	—	0.0340	0.0346	0.0339	0.0345	0.0335

Mean value of $K=0.0341$.*Chloroacetone.*

t	0.000	3.758	5.550	20.550	22.500	24.330
C_t	0.00	6.30	8.66	26.20	27.40	29.35
K	—	0.0715	0.0683	0.0691	0.0661	0.0682

Mean value of $K=0.0686$.*Chloroacetophenone.*

t	0.000	5.100	11.550	15.500	16.333
C_t	0.00	14.56	27.75	34.30	35.45
K	—	0.1336	0.1330	0.1346	0.1345

Mean value of $K=0.1339$.*Bromoacetophenone.*

t	0.000	0.333	0.500	0.667	0.833	1.000	1.333
C_t ...	0.00	37.65	48.00	54.91	60.30	63.75	71.02
K ...	—	7.252	7.382	7.301	7.288	7.035	7.358

Mean value of $K=7.269$.

The following two series of measurements were carried out in 25 per cent. aqueous alcohol (by volume); temperature 55.6° ; initial concentration $N/8$:

Methyl Bromoacetate.

t	0.0000	0.1166	0.2000	0.2835	0.3667	0.4500	0.5333
C_t	0.00	17.60	27.20	34.40	40.00	44.80	48.80
K	—	14.65	14.95	14.81	14.54	14.43	14.30

Mean value of $K=14.61$.*Potassium Bromoacetate.*

t	0.0000	0.2000	0.3667	0.5333	0.7000	0.8568	1.0333
C_t	0.00	18.40	29.60	37.60	44.00	49.60	53.60
K	—	9.02	9.18	9.06	8.98	9.10	9.09

Mean value of $K=9.07$.

The following compounds quoted in the foregoing list are not described in the literature.

Cinnamyl Bromide, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\text{Br}$.—Cinnamyl alcohol was saturated with dry hydrogen bromide at the ordinary temperature, heated to 100° for two hours to decompose the resulting additive product, washed with dilute alkali and with water, dried, and distilled under diminished pressure. It is an almost colourless oil, boiling at $122\text{--}123^\circ/10\text{ mm.}$, insoluble in water, and moderately soluble in organic solvents:

0.1830 gave 0.1752 AgBr. $\text{Br}=40.74$.

$\text{C}_9\text{H}_9\text{Br}$ requires $\text{Br}=40.62$ per cent.

n-Butyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{C}_4\text{H}_9$.—Equimolecular quantities of bromoacetic acid and *n*-butyl alcohol with a few drops of concentrated sulphuric acid were heated to 100° for three hours, the product being washed with dilute alkali and with water, dried, and distilled under diminished pressure. The substance is a colourless liquid, boiling at $78^\circ/10\text{ mm.}$, and is insoluble in water, but miscible with organic solvents; it possesses no sharp odour, thus differing from the other aliphatic esters examined:

0.1085 gave 0.1046 AgBr. $\text{Br}=41.02$.

$\text{C}_6\text{H}_{11}\text{O}_2\text{Br}$ requires $\text{Br}=41.02$ per cent.

tert.-Butyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CMe}_3$.—*tert.*-Butyl iodide was treated with a slight excess of dry silver bromoacetate suspended in ether, the mixture being kept cool. After twelve hours, the ethereal solution was filtered, and the ether distilled off, the residue being fractionated under diminished pressure. A yield of only about 20 per cent. was obtained of a colourless liquid, boiling at $50^\circ/10\text{ mm.}$, insoluble in water, but miscible with organic solvents; it possesses a pungent odour, similar to that of methyl bromoacetate:

0.1747 gave 0.1691 AgBr. $\text{Br}=41.20$.

$\text{C}_6\text{H}_{11}\text{O}_2\text{Br}$ requires $\text{Br}=41.02$ per cent.

Benzyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\text{Ph}$.—Benzyl alcohol and bromoacetic acid were esterified in the manner described under *n*-butyl bromoacetate. The ester is a colourless liquid boiling at $143^\circ/10\text{ mm.}$, and insoluble in water, but miscible with organic solvents; it possesses an odour similar to that of benzyl acetate; the vapour does not attack the mucous membranes at the ordinary temperature:

0.2136 gave 0.1746 AgBr. $\text{Br}=34.82$.

$\text{C}_9\text{H}_9\text{O}_2\text{Br}$ requires $\text{Br}=34.94$ per cent.

Allyl Bromoacetate, $\text{CH}_2\text{Br}\cdot\text{CO}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$.—Allyl alcohol and bromoacetic acid were esterified in the manner described under *n*-butyl bromoacetate. The ester is a colourless liquid, boiling at

73°/10 mm.; it is insoluble in water, but miscible with organic solvents, and possesses an extremely sharp odour:

0.1693 gave 0.1790 AgBr. $\text{Br} = 45.05$.

$\text{C}_5\text{H}_7\text{O}_2\text{Br}$ requires $\text{Br} = 44.69$ per cent.

Diphenylchloroacetamide, $\text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{NPh}_2$. — Diphenylamine, dissolved in dry carbon tetrachloride, was treated with excess of chloroacetyl chloride, the mixture being maintained at atmospheric temperature by immersion in cold water. The precipitated diphenylamine hydrochloride was separated, and the carbon tetrachloride removed from the filtrate by distillation. The residue, after being washed with water, was recrystallised from alcohol. The compound forms colourless needles, melting at 116°, and is moderately soluble in organic solvents:

0.1944 gave 0.1163 AgCl. $\text{Cl} = 14.80$.

$\text{C}_{14}\text{H}_{12}\text{ONCl}$ requires $\text{Cl} = 14.45$ per cent.

In conclusion, the author desires to express his thanks to Assistant-Professor Smiles and to Dr. A. W. Stewart for friendly interest and valuable advice.

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XLVII.—*The Vapour Pressures of Two Perfectly Miscible Solids and their Solid Solutions.*

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IN a former paper (Trans., 1909, **95**, 590) it was shown that camphor and hydroxycamphor or borneol form a continuous series of solid solutions. The vapour pressures of these substances and of their solid solutions have since been measured; the methods employed and results obtained form the subject of the present paper.

The Vapour Pressure of Camphor.

Measurements have previously been made by Ramsay and Young (*Phil. Trans.*, 1884, Part I, 34) and by Allen (Trans., 1900, **77**, 413). Ramsay and Young determined the vapour pressures for temperatures from 0° to 180°. The ordinary barometric method

was employed, and also a second method, in which the temperatures of volatilisation corresponding with different pressures were read on a thermometer the bulb of which was coated with a layer of camphor. This method gave good results for liquids, but does not seem satisfactory when used for solids. Concerning the barometric method, the authors state: "We think it right to give details as to the method of operation, as we found it a matter of extreme difficulty to expel all moisture and air." In spite of the precautions taken, I think it very probable that the results obtained were vitiated by the presence of a trace of air. The results obtained by the two methods are not very concordant, thus at 64° the barometric method gave 6.4 mm., whereas the second method gave 7.2 mm. at 48.9° .

Allen also used two methods, one being the barometric. He took the precaution to boil the mercury, but passed the camphor up in a small tube, and applied a correction for the air admitted.

The air-current method was also employed, the principle of which is to find the weight of camphor required to saturate a known volume of air. The saturation limit was, however, obtained by a method of extrapolation. Allen's work extended over temperatures from 0° to 80° . The vapour pressures measured were very small, the greatest being 9 mm. at 80° . There is considerable discrepancy between Allen's results and those of Ramsay and Young, thus at 48.9° the latter obtained 7.2 mm., whereas Allen at 50° obtained 1.3 mm. I therefore decided to make determinations by both the barometric and air-current methods for temperatures from 78° to 160° .

The Barometric Method.

The apparatus (Fig. 1) consisted of two tubes about 80 cm. long and 12 mm. internal diameter. One of these tubes was provided with a trap 20 cm. from the closed end. This tube served as a standard barometer, which was filled as follows:

Mercury was poured in until it extended a few cm. past the trap. The tube was then connected to the water pump, and the mercury boiled. After cooling, the tube was nearly filled with mercury, and heated to the boiling point of aniline in the vapour-jacket. By connecting to the pump and repeatedly tapping the tube, most of the air bubbles were removed. After cooling, the tube was completely filled and inverted in the trough. The second tube served as the experimental tube. A thick-walled capillary tube was sealed on one end, a piece of wider glass tubing a few mm. diameter next, and then the stopcock.

Both tubes were jacketed. The lower end of the jacket was closed by a doubly-bored rubber cork covered with a layer of

mercury; the upper end by an ordinary split cork. An experiment was conducted as follows. The experimental tube was connected to the pump by sealed glass joints, and the mercury pumped up. The tube was then heated to the boiling point of the liquid in the bulb, the pump kept at work, and the tube repeatedly tapped to remove bubbles from the side. It was then allowed to cool, and the camphor introduced as a small pellet under the mercury in the trough. The tube was again heated, and the pump worked. As the upper part of the tube became hot, the camphor vaporised, and some of it passed into the capillary portion, where it condensed and closed the tube.

When the vapour was condensing well up in the side-tube, the heights of the mercury in the barometer and experimental tube were read by means of a cathetometer, provided with a vernier which enabled readings to be made to 0.01 mm. The telescope of the cathetometer was brought into the horizontal by focussing on the surfaces of the mercury in the limbs of a wide U-tube clamped near the top of the apparatus. Readings were taken until the pressure was constant. The apparatus was then allowed to cool, and readings again taken at room temperature. If the difference in level was now greater than 0.1 mm., the capillary tube was gently heated; the camphor which had condensed there was by this means driven back into the experimental tube or into the upper wider portion, and thus the passage to the pump was again open. The above operations were then repeated until the desired result was obtained.

This made it certain that all the air and moisture had been removed, the vapour pressure of camphor at room temperature being about 0.1 mm. It was found more convenient to make observations at the highest temperature first, as on passing from a lower to a higher temperature air bubbles always appeared on the sides of the tube.

In the early experiments a Töpler pump was used, but later a

FIG. 1.



Fleuss pump was placed at my disposal, and the work became far less tedious. Accurate results at five temperatures were obtained, the temperatures being the boiling points of the following liquids under atmospheric pressure: ethyl alcohol, 78°; propyl alcohol, 96°; toluene, 110°; chlorobenzene, 130°; and bromobenzene, 156°.

The temperatures were read on Anschütz normal thermometers (which had been previously standardised) placed inside the jacket. These could be read to 0.1°. In some cases the temperatures were obtained by reading the barometer, from Ramsay and Young's table of vapour pressures.

The following results were obtained:

Vapour Pressure of Camphor.

Temperature.	Number of readings.	Vapour pressure.
78.0°	30	6.40 mm.
96.8	6	16.15 "
110.9	20	33.00 "
131.1	28	75.37 "
131.4	16	76.00 "
132.0	15	76.61 "
157.0	14	181.50 "

The Vapour Pressure of Borneol.

The vapour pressure of borneol has not been previously measured. It was determined in the same manner with the following results:

Temperature.	Number of readings.	Vapour pressure.
77.9°	6	2.16 mm.
96.8	11	6.65 "
110.0	9	14.94 "
131.0	16	40.92 "
156.0	14	115.16 "

The Air-Current Method.

The apparatus was the same as that used by Perman and Davies in finding the vapour pressures of naphthalene and dilute solid solutions of naphthalene and β -naphthol (Trans., 1907, 91, 1114). Details are given in that paper. A stopcock replaced the ground glass stopper, and a larger bulb was necessary for condensing the camphor. The stopcock was sealed on after introducing the camphor. A thermostat containing water and a toluene regulator were used for temperatures below 100°; for higher temperatures olive oil and a mercury regulator were employed. In order that the pressure of the air in the spiral should be the same before and after the experiment, it was placed in the thermostat and a current of air drawn through for some time; the stopcock was then closed, the spiral removed, the camphor washed out of the bulb with

alcohol and ether, the spiral cleaned by immersing in light petroleum, dried, and weighed. It was again placed in the thermostat, and a known volume of air drawn over, then cleaned and weighed as before.

The temperature of the aspirator and the height of the barometer were observed at the end of the experiment.

Method of Calculation.—If w = weight in grams of camphor withdrawn :

P = pressure of atmosphere in mm.

p = „ air in aspirator in mm.

T = absolute temperature of aspirator.

V = volume of air aspirated, in litres.

v_c = specific volume of camphor vapour = $\frac{22.41}{M}$.

M = molecular weight of camphor.

then, assuming the truth of Dalton's Law of Partial Pressures, the following relationship holds good :

$$\frac{\text{Pressure of camphor vapour}}{\text{Total pressure.}} = \frac{\text{Volume of camphor vapour}}{\text{Total volume.}},$$

or

$$\frac{p_c}{P} = \frac{wv_c}{V + wv_c}$$

correcting volume V for temperature and pressure we get :

$$p_c = \frac{wv_c TP 760}{273 pV + 760 wv_c T'}$$

The following results were obtained :

w .	P (mm.).	V .	p .	T .	Time (mins.).	t° .	p_c (mm.).
0.4169	752.2	7.305	738.7	288.9°	540	77.9	6.823
0.3439	765.0	5.915	752.6	287.5	370	78.0	6.904
0.2522	756.5	4.439	744.2	287.4	325	78.0	6.746
0.3455	763.6	5.915	751.6	287.1	480	78.0	6.923
0.3379	759.8	5.915	747.0	288.2	350	78.0	6.805
0.3355	764.9	5.915	752.2	287.9	330	77.9	6.750
0.2561	763.6	4.439	750.8	288.2	285	78.0	6.872
0.2555	759.9	4.439	746.3	289.0	555	78.0	6.800

Mean vapour pressure at 78° 6.828

0.3956	758.7	2.957	744.9	289.2	180	95.2	15.820
0.3994	759.0	2.957	745.3	289.1	180	95.1	15.961
0.3952	761.2	2.957	747.3	289.3	280	95.1	15.812
0.4016	763.2	2.957	749.1	289.6	250	95.2	16.083
0.3927	765.6	2.957	750.2	291.0	220	95.1	15.835
0.3960	766.1	2.957	750.4	291.3	240	95.1	15.989
0.4005	764.1	2.959	748.4	291.3	270	95.1	15.981
0.3908	766.5	2.959	751.7	290.4	255	95.1	15.711
0.3959	765.4	2.959	750.8	290.2	270	95.1	15.896

Mean vapour pressure at 95° 15.880

<i>w.</i>	<i>P</i> (mm.).	<i>V.</i>	<i>p.</i>	<i>T.</i>	Time (mins.)	<i>t</i> °.	<i>p_c</i> (mm.).
0·3863	760·3	1·4764	746·4	289·3	80	109·0	30·366
0·3870	764·3	1·4764	750·8	288·8	80	109·0	30·347
0·3875	763·3	1·4764	749·7	289·0	80	109·2	30·410
0·3875	762·2	1·4764	748·4	289·2	80	109·0	30·435

Mean vapour pressure at 109° 30·390

1·3500	759·5	2·959	750·0	283·4	135	120·3	50·15
1·3332	762·0	2·959	752·3	283·9	150	120·2	49·67
1·3044	767·1	2·959	758·1	282·7	150	120·0	48·45
1·2940	751·6	2·959	741·8	284·0	180	120·0	48·30

Mean vapour pressure at 120° 48·37

1·0100	746·3	1·4764	736·1	284·6	115	130·4	73·04
1·0064	744·2	1·4764	734·1	284·4	70	130·4	72·78
1·0090	748·5	1·4764	738·7	283·9	70	130·4	72·72

Mean vapour pressure at 130·4° 72·84

0·6859	758·6	1·000	744·6	289·5	60	131·2	74·783
0·6892	759·1	1·000	745·1	289·4	35	131·3	75·090
0·6908	759·5	1·000	745·5	289·5	35	131·3	75·273
0·6928	757·7	1·000	743·4	289·7	40	131·5	75·528

Mean vapour pressure at 131·3° 75·17

1·0352	774·4	1·000	765·7	282·2	55	139·9	104·77
1·0248	773·9	1·000	764·8	282·9	60	139·9	104·12
1·0304	774·1	1·000	764·8	283·3	50	140·1	104·76
1·0204	774·2	1·000	765·6	282·0	50	139·6	103·40

Mean vapour pressure at 140° 104·5

1·5830	765·7	1·000	756·4	282·9	90	150·0	149·83
1·5872	764·0	1·000	754·6	283·3	60	150·0	150·03
1·6014	766·4	1·000	757·7	282·2	45	150·1	150·56

Mean vapour pressure at 150° 150·13

2·0410	758·5	1·000	744·3	298·8	60	156·0	186·43
2·0154	764·0	1·000	750·6	288·8	60	156·0	184·34

Mean vapour pressure at 156° 185·4

It is seen from the above that for temperatures of 120° and upwards, considerable quantities of camphor were drawn off. A larger spiral was used in these experiments. At 150° the camphor showed signs of charring. The rate at which the air was drawn over was varied widely to ensure saturation.

The results obtained by the two methods are compared in the following table:

Temperature.	Barometric (mm.).	Temperature.	Air current (mm.).
78·6°	7·09	78·1°	6·83
96·8	16·15	95·1	15·88
111·0	33·00	110·9	33·00
131·0	75·00	131·1	75·20
157·0	181·5	156·0	185·4

The agreement is very close; the high values given by the air-current method at 150° and 156° are probably due to charring of the camphor. The vapour pressures at the temperatures of Ramsay and Young's experiments and those of Allen have been obtained by graphic interpolation.

These are given in the table below:

Temperature.	Vapour pressure (mm.).	Ramsay and Young (mm.).	Allen (mm.).
78.4°	6.8	9.5 *	7.62
80.0	7.1	—	9.15
92.4	13.1	15.4 *	—
100.0	19.5	22.6	—
101.0	20.5	27.2	—
109.4	30.8	35.0	—
116.7	42.6	46.0	—
127.4	65.5	66.3	—
132.0	76.7	78.1	—
134.2	84.2	88.6	—
136.3	91.0	92.8	—
140.3	105.0	105.0	—
141.7	110.0	109.4	—
147.0	131.0	155.1	—
154.3	165.8	197.6	—

* These results were obtained by the barometric method.

It is seen that the present results are at nearly all temperatures lower than those of the other investigators.

The vapour pressures of borneol were also determined by the air-current method, with the following results:

<i>w.</i>	<i>P.</i>	<i>V.</i>	<i>p</i> (mm.).	<i>T.</i>	Time (mins.).	<i>t</i> ^o .	<i>V.P.</i> (mm.).
0.095	753.7	5.021	742.8	285.7°	390	78.0	2.213
0.1085	755.9	5.021	745.8	284.5	390	78.0	2.344
0.1072	758.8	5.021	749.3	283.6	345	78.1	2.358
Mean vapour pressure at 78°							2.305
0.2912	761.6	5.021	751.5	284.5	255	95.0	6.708
0.2858	758.1	5.021	747.7	284.9	270	95.1	6.597
0.2884	752.3	5.021	741.6	285.4	350	95.3	6.671
0.2908	763.9	5.021	753.2	285.4	300	95.3	6.725
Mean vapour pressure at 95.2°							6.675
0.4105	749.7	3.0024	736.8	285.7	180	110.5	15.765
0.4095	754.1	2.9545	743.2	285.7	180	110.5	15.920
0.3918	751.1	2.9180	740.2	285.7	180	109.8	15.450
0.3528	754.1	2.6185	742.9	286.0	180	110.4	15.508
0.2039	755.5	1.4825	744.3	286.1	180	110.9	15.829
0.2023	765.0	1.4825	752.0	285.8	85	110.4	15.685
Mean vapour pressure at 110.4°							15.72
0.3344	763.3	1.4825	752.1	286.0	60	120.0	25.666
0.3330	752.4	1.4825	741.6	285.5	60	120.0	25.463
0.3286	764.4	1.4825	754.1	284.8	60	120.0	25.045
Mean vapour pressure at 120°							25.371

<i>w.</i>	<i>P.</i>	<i>V.</i>	<i>p</i> (mm.).	<i>T.</i>	Time (mins.).	<i>t</i> °.	<i>V.P.</i> (mm.).
0.5470	765.9	1.4825	756.1	284.0	60	130.4	40.662
0.5397	767.3	1.4825	757.5	284.0	60	130.0	40.148
Mean vapour pressure at 130.2°							40.40
0.6016	770.6	1.00	760.7	284.2	45	139.9	64.181
0.5988	770.4	1.00	760.4	284.3	45	140.1	63.936
Mean vapour pressure at 140°							64.06
0.4738	769.9	0.500	759.8	284.5	45	150.2	96.521
0.4748	769.6	0.500	759.3	284.8	45	150.2	96.814
Mean vapour pressure at 150.2°							96.66
0.6910	768.4	0.500	757.9	285.1	30	159.2	133.31
0.6560	767.7	0.500	757.2	285.1	30	158.4	127.20

These results are compared below with those obtained by the barometric method:

Temperature.	Air current (mm.).	Temperature.	Barometric (mm.).
78.0°	2.30	77.9°	2.16
95.2	6.67	96.8	6.55
110.5	15.70	110.0	15.00
130.2	40.4	131.0	40.92
150.2	96.6	156.0	115.16
158.4	127.2	—	—

As in the case of camphor the results agree closely.

Ramsay and Young have shown that the ratio of the boiling points expressed as absolute temperatures of closely related liquids is constant. As the two solids investigated are also very closely related, the ratios of the absolute temperatures corresponding with equal vapour pressures have been calculated:

Pressure (mm.).	T_c .	T_B .	T_B/T_c .
10	360.3	376.0	1.043
20	373.5	388.4	1.040
30	381.8	396.4	1.038
40	388.3	403.0	1.038
50	393.3	407.8	1.037
60	398.0	411.6	1.034
70	401.3	415.0	1.034
80	405.9	418.0	1.030
90	409.0	421.2	1.030
100	411.8	423.7	1.029
110	415.3	426.3	1.026

The constancy of the ratios is evident.

The Vapour Pressures of Solid Solutions.

One of the chief difficulties of previous investigators has been to obtain solid solutions having vapour pressures large enough to be accurately measured. The only work of importance is that of Speransky (*Zeitsch. physikal. Chem.*, 1903, **46**, 70; 1905, **51**, 45),

who measured the vapour pressures of solid solutions of *p*-dichlorobenzene and *p*-dibromobenzene, and *p*-chlorobromobenzene and *p*-dibromobenzene. He concluded that "the regular laws which hold for liquid solutions also hold for solid solutions."

The Vapour Pressures of Solid Solutions by the Air-Current Method.

The equation given on page 433 for calculating the vapour pressure of camphor, when applied to solid solutions, becomes:

$$P_s = p_c + p_b = \frac{(w_c v_c + w_b v_b)P}{V + w_c v_c + w_b v_b} \quad (1)$$

where

P_s = vapour pressure of solid solution.

p_c and p_b = partial pressures of camphor and borneol.

w_c ,, w_b = weights in grams of camphor and borneol in the total weight (W) drawn off ;

also

$$w_c + w_b = W \quad (2).$$

Equations (1) and (2) contain three unknowns, namely, w_c , w_b , and P_s , hence it seems impossible to determine the vapour pressure of a solid solution, in which both constituents have appreciable vapour pressures, by the air-current method alone. If, however, P_s can be obtained by the barometric method, w_c and w_b can be calculated, and p_c and p_b , the partial pressures of the constituents obtained.

Solving for w_c in this way, we get:

$$w_c = VP_s - Wv_b(P - P_s)/(v_c - v_b)(P - P_s).$$

It is obvious that this involves the difference between the specific volumes v_c and v_b , so that the method can only be applied to cases in which these differ fairly widely.

For camphor and borneol $v_c = 0.1473$ and $v_b = 0.1454$, hence the method is of no use in the present case; we may, however, write $v_c = v_b$ in equation (1), which then becomes:

$$P_s = \frac{Wv_c P}{V + Wv_c},$$

thus the total vapour pressure of a solid solution can be obtained approximately by the air-current method. The error involved is about 1.2 per cent.

A series of experiments was carried out at 110°. The difficulties were now very much greater, as change in concentration had to be avoided as far as possible.

The temperature of 110° was chosen for two reasons: (1) The weight of substance drawn off by aspirating a litre of air through

the spiral was small, and hence the change in concentration of the solution would be small; (2) the vapour pressure at that temperature was large enough to be accurately measured by the barometric method, that for camphor being 33 mm. and for borneol 15 mm.

The solutions were made by fusing the accurately weighed quantities of camphor and borneol in sealed tubes. These were then broken, the mass removed, cut up in small pieces, dried over sulphuric acid, and introduced into the dry spiral. The spiral was placed in the thermostat, and a few c.c. of air drawn through; the stopcock near the condensing bulb was then turned off, the other end of the spiral closed by means of a small india-rubber stopper, the spiral removed, cleaned, and weighed. It was then again placed in the thermostat, and a known volume of air drawn through, again closed, cleaned, and weighed. It was necessary to clean out the spiral after each experiment, and refill with a fresh quantity of solution.

The following results were obtained:

Mols. of borneol per 100 of mixture.	<i>W.</i>	<i>P.</i>	<i>p.</i>	<i>V.</i>	<i>T.</i>	Time (mins.).	<i>t</i> °.	<i>p</i> _s (mm.)
10	0.2632	769.8	765.5	1.00	288.8°	75	110.1°	30.52
	0.2642	750.6	737.5	1.00	288.5	75	110.1	30.62
	0.2645	762.4	749.0	1.00	288.9	75	110.1	30.12
20	0.2404	771.1	758.5	1.00	287.9	90	110.1	27.81
	0.2406	770.7	757.7	1.00	288.3	75	110.1	27.90
30	0.2332	754.2	740.9	1.00	288.8	80	110.0	27.10
	0.2345	755.8	742.4	1.00	288.9	80	110.0	27.26
40	0.2144	747.1	734.7	1.00	287.6	90	110.1	25.21
	0.2154	760.9	747.2	1.00	289.2	110	110.1	24.86
50	0.2054	753.7	740.7	1.00	289.2	110	110.1	24.00
	0.2045	754.8	740.0	1.00	289.3	75	110.0	23.96
60	0.2642	763.5	750.3	1.4825	288.6	100	110.1	20.87
	0.2642	763.5	750.0	1.4825	289.0	150	110.1	20.88
70	0.2510	764.3	750.4	1.4825	294.4	100	110.0	19.93
	0.2510	764.8	750.7	1.4825	289.7	105	110.0	19.94
80	0.2280	765.3	751.9	1.4825	290.0	100	110.1	18.24
	0.2284	765.1	750.5	1.4825	290.2	100	110.1	18.17
90	0.2244	764.3	749.7	1.4825	290.2	90	110.1	17.90
	0.2232	763.8	749.1	1.4825	290.3	100	110.1	17.81
100	0.2662	758.7	744.1	1.00	290.2	90	110.0	15.00
	0.2682	758.7	744.1	1.00	290.2	100	110.0	15.10

Attempts were made to confirm these results by the barometric method. The difficulties were now even greater, and the results can only be regarded as approximate.

To remove air and moisture, to prevent any change in concentration by having a large quantity of substance present, and yet not so much as might obscure the mercury meniscus, was indeed extremely difficult. The experimental tube was now provided with a three-way tap in place of the ordinary stopcock previously used.

The junction of the tube nearest the capillary was well ground on the inside. This enabled the tube to be closed by a ground-glass stopper, sealed to a long glass rod, which passed down the tube beneath the mercury in the trough, being bent at its lower end so that it could be moved from the outside. One branch of the three-way tap communicated with the air pump, the other with a small reservoir of mercury.

The plan was to cause the substance to sublime quite near the top of the tube, keeping the pump at work, then to run in mercury on the top of the ground joint closed by the stopper, and so effectively close the tube.

Experiments with solutions containing 20, 40, 60, and 80 molecules of borneol per 100 molecules of mixture were made. For the experiments with the 20 per cent. solution, a three-way tap and a capillary tube alone were used, mercury being run into the capillary tube. There was some loss by sublimation into the portion outside the vapour jacket, whilst it is certain that air and moisture were removed.

Experiments were made with the same solution at five temperatures, as in the case of the pure substances.

The apparatus had to be taken down and the tube cleaned out before proceeding to make observations with a solution of different concentration, and often for the same solution as the quantity of substance necessary at the high temperatures obscured the mercury meniscus at the lower temperatures.

*Vapour Pressures of Solid Solutions of Camphor and Borneol.
Barometric Method.*

Molecules of borneol per 100 of mixture = 20.

Temperature.	Number of readings.	Vapour pressure.
78.6°	5	6.10 mm.
97.0	4	15.90 "
97.4	6	16.04 "
110.6	15	28.13 "
131.6	4	66.90 "
131.8	6	67.50 "
156.2	6	159.40 "

Molecular Concentration = 40 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.4°	5	5.54 mm.
97.2	5	13.27 "
110.0	5	25.60 "
131.0	5	63.70 "
156.4	5	150.5 "

Molecular Concentration = 60 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.5°	7	4.83 mm.
97.1	6	11.40 "
110.2	5	23.05 "
131.2	5	60.58 "
156.0	7	140.00 "

Molecular Concentration = 80 per cent. borneol.

Temperature.	Number of readings.	Vapour pressure.
78.6°	6	3.56 mm.
96.8	4	8.80 "
97.1	5	9.10 "
110.6	4	19.70 "
110.8	4	20.00 "
131.8	4	56.40 "
156.2	10	130.20 "

These results, as well as those for camphor and borneol, have been plotted on a temperature-pressure diagram (Fig. 2); it is seen that the curves for the solutions lie between those for the pure substances. The vapour pressures obtained by both methods are compared in the following table:

Concentration.	Temperature.	Barometric (mm.).	Temperature.	Air current (mm.).
20 mols. borneol	110.6°	28.1	110.1°	27.8
40 " "	110.0	25.6	110.1	25.0
60 " "	110.2	23.0	110.8	20.8
80 " "	110.6	19.7	110.1	18.2

The deviations are in the direction expected, since the errors are entirely due to change in concentration. For those solutions relatively richer in camphor, the barometric method would give, owing to loss of the more volatile component, results which would be too low, and conversely for solutions relatively richer in borneol. The agreement is as close as can be expected, considering the extreme difficulty of determining the vapour pressure of a solid solution by the barometric method.

Isothermals are shown in Fig. 3. The results given at 110° are those obtained by the air-current method; for other temperatures, the barometric results are given. It is seen that the isothermals

FIG. 2.

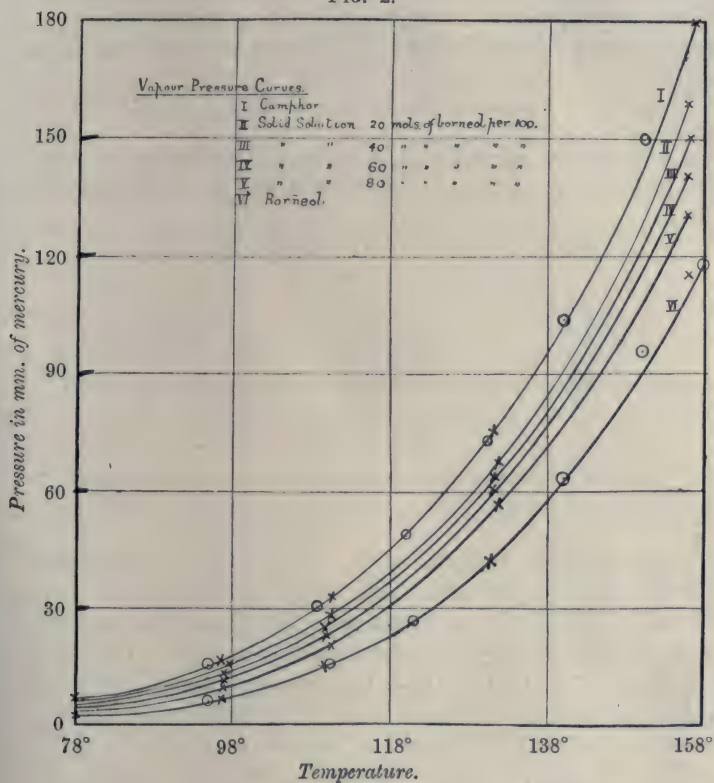
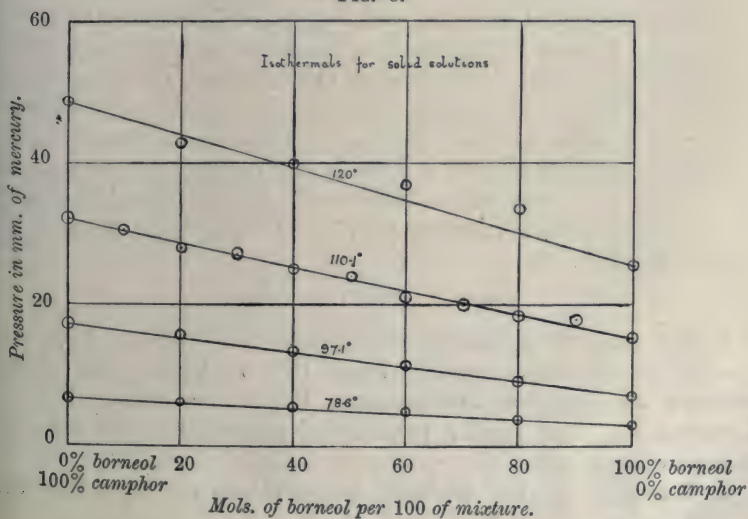


FIG. 3.



are straight lines. This leads to the important conclusion "that the vapour pressure of a solid solution is a linear function of the molecular concentration, and can be calculated from the equation:

$$P_s = \frac{nP_B + (100 - n)P_c}{100},$$

where n = number of mols. of borneol per 100 mols. of mixture.

The calculated and observed results are given in the following table:

Vapour Pressure of Solid Solutions at 110°.

Concentration.	Calculated.	Observed (air-current method).
10	30.3 mm.	30.4 mm.
20	28.6 "	27.8 "
30	26.9 "	27.1 "
40	25.2 "	25.0 "
50	23.5 "	24.0 "
60	21.8 "	20.9 "
70	20.1 "	19.9 "
80	18.4 "	18.2 "
90	16.7 "	17.9 "

Speransky (*ibid.*), for solid solutions of *p*-chlorobromobenzene and *p*-dibromobenzene, obtained fairly good agreement between calculated and observed vapour pressures. The pressures were measured in mm. of paraffin oil in a differential tensimeter. Young (Trans., 1902, **81**, 768) has shown that the equation given above holds for mixtures of liquids which are chemically closely related, hence the present work is strong evidence in support of the van't Hoff theory of solid solutions, that they follow the same laws as liquid solutions. It is seen also from the curves in Fig. 2 that the vapour pressures of solid solutions of camphor and borneol are always greater than the vapour pressure of borneol. Precisely the same may be said of the freezing points, hence, when the substance of lower freezing point and vapour pressure is considered, the addition of a substance with which it forms solid solutions produces a change in these properties opposite to that expected, and directly contrary to that which usually occurs with solutions which obey Raoult's law. It seems therefore futile to apply such laws to determine the molecular weight of solids.

Summary and Conclusion.

1. The vapour pressures of camphor and borneol have been determined for temperatures from 78° to 156°. The results obtained for camphor are generally lower than those of former investigators. The vapour pressure of borneol has not been previously determined.

2. The ratio of the absolute temperatures corresponding with

equal vapour pressures is constant, thus Ramsay and Young's rule for closely related liquids also holds for closely related solids.

3. The air-current method of determining vapour pressures has been extensively used, and it has been shown that the results obtained agree closely with those obtained by the barometric method.

4. The vapour pressures of a complete series of solid solutions have been determined. It has been shown that the vapour pressures of solid solutions, like other physical properties, follow the ordinary mixture law:

$$p_s = \frac{np_A + (100 - n)p_B}{100},$$

where n = number of mols. of A per 100 of mixture.

5. Approximate results for solid solutions have been obtained by the barometric method, more accurate results by the air-current method.

6. A method of determining the partial pressures of solutions by combining the data obtained from barometric and air-current methods has been indicated.

7. Since the vapour pressures of solid solutions of camphor and borneol follow the mixture law, it is highly probable that the molecular weights of the solid components are normal.

8. The agreement between the results obtained by the two methods leads to the conclusion that the densities of the vapours of camphor and borneol at the temperatures employed are normal.

In conclusion, I wish to express my thanks to the Principal of University College, Cardiff, and the staff of the chemical department, for the interest taken in the work and the facilities afforded me. I am especially grateful to Dr. E. P. Perman for suggesting the work, and for his advice and assistance in carrying it out. The expenses of the work have been defrayed by grants from the Glamorgan County Council and the College Council, to whom also I wish to express my thanks.

UNIVERSITY COLLEGE,
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XLVIII.—*Salts and Ethers of 2:3:5-Trinitro-4-acetylaminophenol.*

By RAPHAEL MELDOLA, F.R.S., and HAROLD KUNTZEN.

THE marked acid character of the above compound, which was first described by one of the authors in 1906 (Trans., **89**, 1935), is shown by the readiness with which it forms metallic and organic salts. At the same time, the extreme mobility of one of the nitro-groups tends to bring about decomposition of the salts, especially in presence of excess of base. With organic bases of the nature of primary amines, the trinitro-compound, as stated in former papers, readily forms salts, but these pass rapidly into catenation products and finally into iminazoles, so that the intermediate product generally consists of a mixture of the salts of the trinitro-compound with those of the catenation product, or of the iminazole, or of both. With respect to metallic salts, it was pointed out in a recent communication (Trans., 1909, **95**, 1381) that these could be safely prepared by the interaction of the trinitro-compound and salts of metals with weak acids. This principle has now been successfully applied for the preparation of a number of metallic and organic salts from the acetates, carbonates, etc., of the respective metals or alkaloids. Details of the mode of preparation of the various salts are given in the experimental part of this paper, the series described comprising those which are sufficiently insoluble in water to crystallise from the hot concentrated solution on cooling. This series is, however, quite typical, and the research has not been extended to those more soluble salts (lithium, calcium, etc.) which could not be directly isolated in the manner described, but which could no doubt be obtained if wanted by the evaporation of their solutions in a vacuum at the ordinary temperature.

General Characters of the Salts.

The metallic salts of trinitroacetylaminophenol are all highly coloured, red substances, the parent compound being pale yellow.* It is for this, among other reasons, that these salts have been considered of sufficient interest to form the subject of a special study in view of the large amount of work which has of late years been bestowed upon the subject of colour in relation to chemical constitution. It has already been pointed out that the trinitro-compound is capable of a double "isonitro-" isomerism (Trans.,

* The lead salt alone approaches the free trinitro-compound in colour.

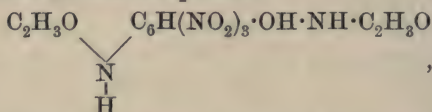
1908, **93**, 1662), so that a change in constitution in passing from the free compound to the salt might reasonably be postulated. As satisfactory evidence of such change was most likely to be furnished by a study of the absorption spectra, and as Dr. J. T. Hewitt has recently been dealing with this subject (Trans., 1909, **95**, 1755), he has, at our request, been good enough to photograph the absorption spectra of the free compound and its salts, and his observations are appended to the present paper. As will be seen from these results, there is justification for the belief that in forming a salt the *isonitro*-constitution is acquired, and he has further obtained evidence of the transitory existence of a disodium salt in presence of excess of alkali. In connexion with these results, it is of interest to note that the methyl ether described in this paper (2:3:5-trinitro-4-acetylaminoisole) is, to the eye, a colourless substance, and therefore may be presumed to have the same constitution as the free trinitro-compound.

All the metallic salts of trinitroacetylaminophenol now made known are very soluble in water. They are beautifully crystalline, and contain water of crystallisation which in most cases cannot be expelled at 100°, and at higher temperatures decomposition takes place. They all deflagrate on heating in the dry state, but not explosively, the only exception being the cobalt salt, which deflagrates more sharply than any of the others.

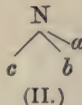
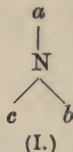
In forming salts with natural alkaloids, the trinitro-compound shows marked preferential characters. With brucine and guanidine very stable insoluble salts separate at once on mixing solutions of the trinitro-compound and the base, or by the action of the trinitro-compound on the acetate of the base. Narcotine forms a less stable salt, whilst carbamide, theobromine, quinine, strychnine, cinchonine, and morphine do not give readily isolable salts. Caffeine forms a salt which is interesting as being dissociable in alcoholic solution. If equimolecular weights of the base and the trinitro-compound are dissolved in a small quantity of boiling alcohol, the solution, on cooling, deposits at first crystals of caffeine, and subsequently a mixture of caffeine and the caffeine salt, the latter crystallising in yellow, nodular aggregates. Further crystallisation of the mixed crystals leads to the same result, even when excess of trinitro-compound is intentionally added, so that the pure caffeine salt could not be isolated. In alcoholic solution there appears to be an equilibrium mixture, varying in composition with temperature and concentration, of free caffeine, free trinitro-compound, and caffeine salt.

Attempt to Prepare an Optically Active Compound Containing an Asymmetric Tervalent Nitrogen Atom.

The main object in studying the salts formed by the trinitro-compound with natural alkaloids was to test a somewhat plausible hypothesis which had suggested itself with respect to the possible asymmetry of the nitrogen atom in the trinitro-compound itself. From the formula of this compound,



it will be seen that the nitrogen atom is combined with two acid radicles (acetyl and the substituted trinitro-phenol residue) and one positive atom (hydrogen). In most of the attempts that have hitherto been made to resolve tervalent nitrogen compounds, the nitrogen atom has been combined with positive radicles, and the molecule as a whole has been basic in character.* The negative results have in these cases been attributed to racemisation due to hydrolytic dissociation of the salt or to the temporary assumption of quinquivalent function by the nitrogen atom. The trinitro-compound under investigation is certainly free from the latter objection, as it is strongly acid in character, and does not form salts with acids. On the other hand, disregarding for the present the possibility of hydrolytic dissociation, if there is any weight attaching to the hypothesis of mutual attractions and repulsions between the radicles in a molecule, it might be considered that three positive radicles attached to a nitrogen atom would by mutual repulsion favour the configuration sometimes assigned to such compounds (No. I), the "bonds" being in one plane:



When two strongly acid radicles and one positive atom are present it seemed, on this view, that every chance for displacement of the "bonds" would be given, and the asymmetric configuration (No. II) assumed. At any rate, the hypothesis seemed sufficiently plausible to be worth submitting to the test of experiment. The result, as

* By way of exception to this general statement, the attempt by Jones and Millington to resolve methylethylanilinesulphonic acid may be referred to (*Proc. Camb. Phil. Soc.*, 1904, 12, 489). In this case, also, the result was negative.

in former cases, was, however, negative. A specimen of the brucine salt was prepared by precipitating the trinitro-compound in alcoholic solution with a semi-molecular proportion of the base. The trinitro-compound recovered from the filtrate and from the salt by decomposition by acid was examined for us by Dr. T. Martin Lowry, but in neither specimen was there any trace of optical activity. Dr. Lowry reports that he made his observations with the acetone solution of the compound (4 grams per 100 c.c. in 2-dcm. tubes) by means of red (lithium) light. We desire to take this opportunity of expressing our thanks to Dr. Lowry for the assistance thus rendered.

Although the result is in this case negative, we propose continuing the investigation, as there still remains the possibility that the asymmetry may exist only while the trinitro-compound and the base are in combination.* To test this point, it will be necessary to prepare some salt more soluble than the brucine salt, and to compare its optical activity in some non-hydrolysing solvent with that of the base with which the trinitro-compound is combined.

EXPERIMENTAL

Ammonium Salt, $C_8H_6O_8N_4 \cdot NH_3$.

Prepared by dissolving the trinitro-compound in a hot concentrated solution of ammonium acetate and allowing to crystallise. Bright red, spherical aggregates of slender needles. The salt is anhydrous, and undergoes decomposition at about 203° when heated in a capillary tube:

0.0434 gave 8.6 c.c. N_2 (moist) at 12° and 761.3. $N = 23.56$.

$C_8H_6O_8N_5$ requires $N = 23.10$ per cent.

Sodium Salt, $C_8H_5O_8N_4Na, 3H_2O$.

Prepared by dissolving the trinitro-compound in a hot concentrated solution of sodium carbonate. The salt separates slowly on cooling in long, transparent, ruby-red prisms. Professor W. J. Pope, who has been good enough to examine these crystals for us, reports that they "probably belong to the anorthic system. The acute bisectrix of a large axial angle emerges through the small end faces; the optic axial dispersion is marked, and the angle for blue is larger than that for red light":

0.1336 gave 17.55 c.c. N_2 (moist) at 12.2° and 747 mm. $N = 15.31$.

0.1132 ,, 0.0220 Na_2SO_4 . $Na = 6.31$.

$C_8H_5O_8N_4Na, 3H_2O$ requires $N = 15.47$; $Na = 6.36$ per cent.

* As bearing on this point, see a paper by Pope and Harvey (Trans., 1901, 79, 837).

On heating in the water-oven, the salt becomes opaque and brick-red in colour, and loses weight owing to dehydration and (possibly) partial decomposition, the loss of weight being somewhat in excess of that required by the $3\text{H}_2\text{O}$ indicated by the above analyses:

0.5486, heated in the water-oven, lost $0.0930 = 16.95$ per cent.

0.0506 (dried as above) gave 7.75 c.c. N_2 (moist) at 12° and 750.1 mm. $\text{N} = 18.01$.

0.1036 (dried as above) gave $0.0238 \text{Na}_2\text{SO}_4$. $\text{Na} = 7.45$.

$\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{Na}$ requires $\text{N} = 18.19$; $\text{Na} = 7.48$ per cent. A loss of $3\text{H}_2\text{O}$ requires 14.9 , and of $3\frac{1}{2}\text{H}_2\text{O}$ 17.43 per cent.

Potassium Salt, $\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$.

This salt has already been described (Trans., 1909, **95**, 1381). To the former description we are now enabled to add that an anhydrous salt is formed on long exposure to the air at the ordinary temperature:

0.0678 gave 10.2 c.c. N_2 (moist) at 17° and 755.5 mm. $\text{N} = 17.31$.

0.0928 „ $0.0244 \text{K}_2\text{SO}_4$. $\text{K} = 11.81$.

$\text{C}_8\text{H}_5\text{O}_8\text{N}_4\text{K}$ requires $\text{N} = 17.28$; $\text{K} = 12.07$ per cent.

Barium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Ba}, 3\text{H}_2\text{O}$.

This salt was prepared by two methods, first by dissolving the trinitro-compound in a hot solution of barium acetate, and secondly, by boiling the trinitro-compound with barium carbonate and water and filtering from excess of barium carbonate. In both cases the solution deposits the salt on cooling as flat needles of a deep red colour and having a slight metallic reflex in the mother liquor when viewed at an angle. The analyses of the specimens prepared by the barium acetate method were somewhat irregular, and indicate that a more definite salt is given by the other method:

0.0550 gave 7.15 c.c. N_2 (moist) at 19° and 758.5 mm. $\text{N} = 14.9$.

0.1099 „ 13.9 c.c. N_2 (moist) at 11.5° and 754.1 mm. $\text{N} = 14.92$.

0.0770 „ 0.0238BaSO_4 . $\text{Ba} = 18.19$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Ba}, 3\text{H}_2\text{O}$ requires $\text{N} = 14.71$; $\text{Ba} = 18.0$ per cent.

The salt does not lose weight on drying at 100° .

Magnesium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Mg}, 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and magnesium acetate. Bright red prisms. The specimen analysed was twice crystallised from water:

0.1292 gave 17.85 c.c. N_2 (moist) at 18.5° and 753.4 mm. $\text{N} = 15.78$.

0.1122 gave 0.0161 $\text{Mg}_2\text{P}_2\text{O}_7$. $\text{Mg}=3.21$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Mg}, 6\text{H}_2\text{O}$ requires $\text{N}=15.95$; $\text{Mg}=3.03$ per cent.

The salt does not lose water at 100° .

Zinc Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Zn}, 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and zinc acetate. Bright red prisms, resembling the magnesium salt:

0.1633 gave 21.1 c.c. N_2 (moist) at 18° and 760 mm. $\text{N}=14.92$.

0.3240 „ 0.0352 ZnO . $\text{Zn}=8.73$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Zn}, 6\text{H}_2\text{O}$ requires $\text{N}=15.05$; $\text{Zn}=8.8$ per cent.

The salt does not lose weight at 100° .

Cadmium Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Cd}, 6\text{H}_2\text{O}$.

Prepared by boiling the trinitro-compound with water and cadmium carbonate, filtering from excess of carbonate, and allowing to cool, when the salt crystallises out in red scales:

0.1422 gave 16.9 c.c. N_2 (moist) at 13° and 765.3 mm. $\text{N}=14.15$.

0.1602 „ 0.0262 CdO . $\text{Cd}=14.32$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Cd}, 6\text{H}_2\text{O}$ requires $\text{N}=14.17$; $\text{Cd}=14.22$ per cent.

The salt darkens in colour and shows signs of fusion and decomposition when heated in the water-oven.

Nickel Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Ni}, 4\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and nickel carbonate. The salt separates as dark brick-red prisms:

0.160 gave 22.3 c.c. N_2 (moist) at 14° and 745.8 mm. $\text{N}=16.08$.

0.2460 „ 0.0260 NiO . $\text{Ni}=8.31$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Ni}, 4\text{H}_2\text{O}$ requires $\text{N}=15.99$; $\text{Ni}=8.37$ per cent.

The salt undergoes no change at 100° . It deflagrates somewhat sharply when heated in the dry state.

Cobalt Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Co}, 6\text{H}_2\text{O}$.

Prepared as above from the trinitro-compound and cobalt carbonate. Crystallises in bright red prisms:

0.1899 gave 24.2 N_2 (moist) at 11° and 764.3 mm. $\text{N}=15.24$.

0.1714 „ 0.0135 Co . $\text{Co}=7.88$ per cent.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Co}, 6\text{H}_2\text{O}$ requires $\text{N}=15.2$; $\text{Co}=8.1$ per cent.

This salt differs from the nickel salt, not only in the quantity of water of crystallisation with which it combines, but also in the readiness with which it parts with this water. When heated in the water-oven, the salt becomes of a dark brick-red colour, and

loses practically all its water. The anhydrous salt becomes hydrated, and changes to a bright red colour on moistening with water:

0.5032, dried in water-oven, lost 0.071. $\text{H}_2\text{O}=14.11$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Co}, 6\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=14.66$ per cent.

0.0529 (dried as above) gave 7.85 c.c. N_2 (moist) at 9° and 749.6 mm. $\text{N}=17.6$.

0.0446 (dried as above) gave 0.0042 Co. $\text{Co}=9.44$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Co}$ requires $\text{N}=17.82$; $\text{Co}=9.38$ per cent.

This salt, on heating, deflagrates more sharply than the nickel salt.

Manganese Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Mn}, 4\text{H}_2\text{O}$.

Prepared as before from the trinitro-compound and manganese carbonate. Dull red, rhombohedral prisms:

0.2152 gave 29.2 c.c. N_2 (moist) at 12.3° and 749.9 mm. $\text{N}=15.9$.

0.1266 „ 0.0132 Mn_3O_4 . $\text{Mn}=7.51$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Mn}, 4\text{H}_2\text{O}$ requires $\text{N}=16.08$; $\text{Mn}=7.89$ per cent.

The salt darkens and shows signs of fusion and decomposition when heated in the water-oven.

Copper Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Cu}, 4\text{H}_2\text{O}$.

Prepared from the trinitro-compound and copper carbonate as before. Dull brick-red, transparent, rhombohedral prisms:

0.1273 gave 17.1 c.c. N_2 (moist) at 12° and 745.1 mm. $\text{N}=15.63$.

0.1709 „ 0.0190 CuO . $\text{Cu}=8.89$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Cu}, 4\text{H}_2\text{O}$ requires $\text{N}=15.88$; $\text{Cu}=9.0$ per cent.

The salt becomes light brown and opaque on heating in the water-oven, and partly loses its water. Complete dehydration could not be effected without decomposition:

0.5247 lost 0.0528. $\text{H}_2\text{O}=10.06$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Cu}, 4\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=12$ per cent.

The salt thus dried gave the following results on analysis:

0.0874 gave 13.1 c.c. N_2 (moist) at 12° and 755 mm. $\text{N}=17.68$.

0.0844 „ 0.0104 CuO . $\text{Cu}=9.84$.

$\text{C}_{16}\text{H}_{10}\text{O}_{16}\text{N}_8\text{Cu}$ requires $\text{N}=17.69$; $\text{Cu}=10.03$ per cent.

Lead Salt, $(\text{C}_8\text{H}_5\text{O}_8\text{N}_4)_2\text{Pb}, 3\text{H}_2\text{O}$.

Prepared from lead carbonate and the trinitro-compound as above. Flat, orange needles:

0.0948 gave 10.75 c.c. N_2 (moist) at 11.5° and 752.2 mm. $N=13.36$.

0.1428 „ 0.0525 $PbSO_4$. $Pb=25.16$.

$C_{16}H_{10}O_{16}N_8Pb, 3H_2O$ requires $N=13.48$; $Pb=24.89$ per cent.

This salt does not lose water at 100° .

Thallium Salt, $C_8H_5O_8N_4Tl$.

From the trinitro-compound and thallium carbonate by the same method. Brick-red, fern-like leaflets:

0.0779 gave 7.6 c.c. N_2 (moist) at 7.7° and 741.4 mm. $N=11.52$.

0.1577 „ 0.0770 $TlCl$. $Tl=41.60$.

$C_8H_5O_8N_4Tl$ requires $N=11.46$; $Tl=41.72$ per cent.

The salt undergoes no change at 100° .

Silver Salt, $C_8H_5O_8N_4Ag, 3H_2O$.

The salt was prepared from the trinitro-compound and silver carbonate by the method described above. It generally crystallises in red prisms, but sometimes separates as orange-red scales. The analysis of the salt offered considerable difficulty, as the free trinitro-compound appears to interfere with the precipitation of the silver chloride. Good results were only obtained when the organic matter was destroyed by heating the salt in a sealed tube with fuming nitric acid for three hours at 190° . The water could not be completely expelled by heating in the water-oven; at this temperature the salt darkens, and, on long heating, shows signs of decomposition. About 102° the salt deflagrates:

0.0622 (air dried) gave 6.8 c.c. N_2 (moist) at 14° and 744.2 mm. $N=12.59$.

0.2996 (air dried) gave 31 c.c. N_2 (moist) at 12° and 768 mm. $N=12.38$.

0.2570 gave 0.0820 $AgCl$. $Ag=24.02$.

$C_8H_5O_8N_4Ag, 3H_2O$ requires $N=12.53$; $Ag=24.14$ per cent.

A specimen dried in the water-oven gave the following results:

0.0682 gave 8.2 c.c. N_2 (moist) at 14° and 730.5 mm. $N=13.58$.

0.0564 „ 0.0201 $AgCl$. $Ag=26.82$.

$C_8H_5O_8N_4Ag$ requires $N=14.26$; $Ag=27.46$ per cent.

The salt is not only readily soluble in water, but also in methyl and ethyl alcohols, and by its means the methyl ether has been prepared, and is described in the present paper.

Brucine Salt, $C_8H_6O_8N_4, C_{23}H_{26}O_4N_2$.

This salt was prepared by adding to a hot saturated solution of the alkaloid in absolute alcohol an equimolecular proportion of the

trinitro-compound dissolved in the same solvent. It was also obtained by dissolving the trinitro-compound in a hot aqueous solution of brucine acetate and allowing to cool. In both cases the same salt is obtained. It is practically insoluble in alcohol, so that the trinitro-compound might be used as a precipitant for the base. It can be best purified by dissolving in hot glacial acetic acid, which does not appear to decompose the salt, diluting the solution with water, and allowing to crystallise. It separates, on cooling, in rosettes of deep reddish-brown needles, which appear ruby-red by transmitted light. The salt melts with decomposition at $222-224^{\circ}$:

0.2180 gave 0.4366 CO_2 and 0.0906 H_2O . $\text{C}=54.62$; $\text{H}=4.89$.

0.1322 „ 0.2648 CO_2 „ 0.0572 H_2O . $\text{C}=54.62$; $\text{H}=4.80$.

0.1268 „ 13.7 c.c. N_2 (moist) at 21° and 757.5 mm. $\text{N}=12.26$.

$\text{C}_{31}\text{H}_{32}\text{O}_{12}\text{N}_6$ requires $\text{C}=54.68$; $\text{H}=4.74$; $\text{N}=12.36$ per cent.

In connexion with this salt it is of interest to note that brucine also forms a very insoluble picrate.

Guanidine Salt, $\text{C}_8\text{H}_6\text{O}_8\text{N}_4, \text{CH}_5\text{N}_3$.

This salt was prepared by dissolving guanidine carbonate in dilute acetic acid and saturating the hot solution with the trinitro-compound, the latter being added in small portions in the solid state. The salt crystallises out on cooling in dark brown needles, appearing ruby-red by transmitted light, and having a bronzy lustre when seen by reflected light. Purification was effected by crystallisation from hot water, in which the salt dissolves with an orange colour:

0.1781 gave 44.55 c.c. N_2 (moist) at 20.5° and 754.1 mm. $\text{N}=28.32$.

0.2170 „ 0.2502 CO_2 and 0.0650 H_2O . $\text{C}=31.44$; $\text{H}=3.32$.

$\text{C}_9\text{H}_{11}\text{O}_8\text{N}_7$ requires $\text{C}=31.29$; $\text{H}=3.21$; $\text{N}=28.41$ per cent.

The salt is quite stable; the melting point is 227° , and no loss of weight takes place at 100° .

Narcotine Salt, $\text{C}_8\text{H}_6\text{O}_8\text{N}_4, \text{C}_{22}\text{H}_{23}\text{O}_7\text{N}$.

This salt was prepared from the trinitro-compound and the acetate of the base, or by mixing alcoholic solutions of the components in the usual way. Some difficulty was experienced in obtaining a pure product owing to the tendency of the salt to dissociate when crystallised from alcohol. The most satisfactory results on analysis were given by specimens crystallised from alcohol in the presence of a slight excess of the base:

0.0988 gave 0.1860 CO_2 and 0.0378 H_2O . $\text{C}=51.34$; $\text{H}=4.35$.

0.1348 „ 0.2552 CO_2 „ 0.0504 H_2O . $\text{C}=51.63$; $\text{H}=4.16$.

0.0358 gave 3.1 c.c. N_2 (moist) at 12° and 761.3 mm. $N = 10.30$.

$C_{30}H_{29}O_{15}N_5$ requires $C = 51.48$; $H = 4.19$; $N = 10.02$ per cent.

The salt crystallises in flat, yellow needles, melting at $193-194^\circ$.

Caffeine Salt, $C_8H_6O_8N_4, C_8H_{10}O_2N_4$.

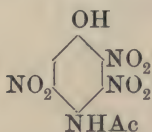
Although, for reasons stated in the introductory portion of this paper, the pure salt could not be isolated, the analytical results all pointed to the above formula. The salt, freed as far as possible from admixed caffeine, crystallises in rosettes of yellow needles, melting at about 177° .

Dr. J. T. Hewitt's Observations on the Absorption Spectrum of Trinitroacetylaminophenol and its Salts.

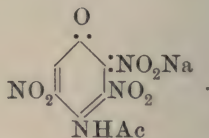
The pale yellow trinitro-compound dissolves both in water and 96 per cent. alcohol, with an intense yellow colour, inclining to orange. Whilst this orange shade is deepened by the addition of dilute sodium hydroxide or sodium acetate, the colour in the latter case soon reaching a maximum, hydrogen chloride has an opposite effect, comparatively small quantities causing the solution to assume a pale yellow tint comparable with that of the solid compound. This result is quite in accordance with the fact that trinitroacetylaminophenol is a fairly strong acid, and necessitates the addition of a highly ionised acid, such as hydrogen chloride, to the alcoholic solution if the spectrum of the non-ionised nitrophenol is to be observed (compare Buttler and Hewitt, *Trans.*, 1909, **95**, 1755, *et seq.*). In these circumstances the principal feature of the absorption spectrum was a band having its head at an oscillation frequency of about 2800, and not differing very markedly in this respect or in its persistency from that observed by Hartley and Huntington in the case of *o*-nitrophenol (see the curves plotted on a logarithmic scale by Baly, Edwards, and Stewart, *Trans.*, 1906, **89**, 519).

When an alcoholic solution to which a dilute alcoholic solution of sodium acetate has been added until no further intensification of the orange shade is noticeable (solution of the monosodium salt), a spectrum is obtained which in one respect shows a marked similarity to that observed by Baly and his co-workers (*loc. cit.*) in the case of the sodium salt of *o*-nitrophenol, and by Buttler and Hewitt (*loc. cit.*, p. 1756) with that of 2:6-dinitrophenol, the band of slowest vibration having its head at an oscillation frequency of 2250. Hence it seems justifiable to conclude that, as in the case of *o*-nitro- and 2:6-dinitro-phenols, formation of the sodium salt is accompanied by an alteration in structure, the trinitroacetylami-

phenol and its sodium salt being related in the sense of the formulæ:



and



On the physical side there seems but little doubt that a radical alteration in absorption on formation of a derivative is accompanied by a radical alteration in structure, although it is well to keep in mind that the only direct *chemical* evidence bearing on the assumed change of structure on salt formation (or ionisation) in the case of the nitrophenols depends on the isolation of highly coloured *aci*-esters by Hantzsch and Gorke (*Ber.*, 1906, **39**, 1073).

If to a solution (aqueous or alcoholic) of the trinitro-compound, alkali be added in excess, a deep purple-red colour is produced; such solutions are, however, unstable, the decomposition making itself manifest by a deposition of sodium salt (? nitrite) when a solution in 96 per cent. alcohol is examined, and a change of colour towards yellow. Despite this inconvenience, an attempt was made to photograph the absorption spectrum of a freshly prepared solution, which very possibly contains a disodium salt: the persistency of the colour band was very similar to that found for a monosodium salt, but the head lies at an oscillation frequency of about 2040.

The curves in the figure were obtained with solutions made up in the following manner.

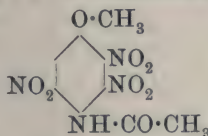
Trinitroacetylaminophenol (full curve).—A *N*/1000-solution was prepared from 0.0286 gram and 5 c.c. of fuming hydrochloric acid, made up to 100 c.c. with 96 per cent. alcohol. A *N*/10,000-solution was prepared by diluting 10 c.c. of the *N*/1000-solution and 5 c.c. of fuming hydrochloric acid to 100 c.c. with 96 per cent. alcohol.

Monosodium Salt (dotted curve).—0.0286 Gram of the phenol was dissolved in alcohol, a solution of sodium acetate added in at least twice the excess of that necessary to produce any further intensification of the orange shade, and then made up to 100 c.c. with alcohol. 5 mm. of this *N*/1000-solution gave the same absorption as 50 mm. of the solution obtained on tenfold dilution (*N*/10,000). This shows that any hydrolysis of the salt is inappreciable, as might have been expected.

Excess of Alkali.—The solution photographed was obtained by dissolving 0.0286 gram of trinitroacetylaminophenol in alcohol, adding alcoholic sodium hydroxide in excess of that required for maximum development of the purple shade, and making up to 100 c.c. with 96 per cent. alcohol. As 5 mm. of such a solution did

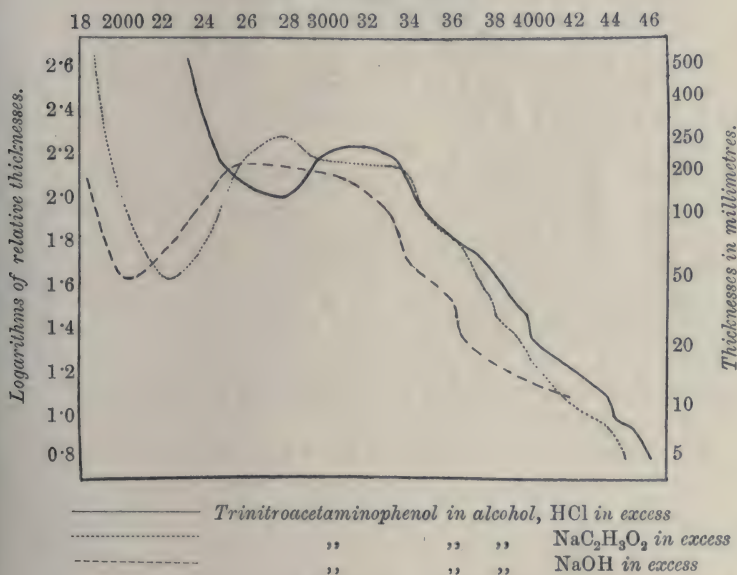
not give the same absorption as 50 mm. of a *N*/10,000-solution, only the stronger solution was used. The salt containing more than one atom of metal is evidently strongly hydrolysed on dilution.

Methyl Ether=2:3:5-Trinitro-4-acetylaminoisole,



Attempts to methylate the trinitro-compound by silver oxide and methyl iodide led to negative results (Trans., 1909, **95**, 1379). The

Oscillation frequencies.



isolation of the silver salt described in this paper has, however, rendered possible the preparation of the above methyl ether and the corresponding trinitroanisidine. The silver salt in methyl-alcoholic solution is rapidly decomposed by methyl iodide, even at the ordinary temperature, the separation of silver iodide commencing soon after mixing the solutions and being complete after about half an hour's heating on the water-bath. Only about 15 per cent. of the trinitro-compound undergoes methylation in this process. The alcoholic solution, after filtration, is evaporated to a small volume, diluted with water, and extracted with an aqueous solution of

sodium acetate to remove the unmethylated portion. The residue, after crystallisation from alcohol, consists of white needles, melting at 194° :

0.0566 gave 8.9 c.c. N_2 (moist) at 13.5° and 762.8 mm. $N=18.61$.

$C_9H_8O_8N_4$ requires $N=18.67$ per cent.

That the compound has the above constitution is proved by boiling its alcoholic solution for a short time with a little aniline, removing the excess of aniline by dilute hydrochloric acid, anhydridising the dry product by heating with a little acetic anhydride, and purifying the iminazole thus obtained by crystallisation from alcohol. The compound was identified as the methyl ether (m. p. $205-206^{\circ}$) of dinitrohydroxy-1-phenylmethylbenzimidazole described in a former paper (Trans., 1908, **93**, 1672):

0.1074 gave 15.9 c.c. N_2 (moist) at 12° and 743 mm. $N=17.17$.

$C_{15}H_{12}O_5N_4$ requires $N=17.07$ per cent.

As the melting point of the acetyl derivative of the trinitroanisidine recently obtained by Reverdin (*Arch. Sci. phys. nat.*, 1909, **27**, 396; **28**, 381) is quite different from ours, namely, 242° , Reverdin's compound is no doubt a derivative of the isomeric 2:3:6-trinitroanisidine. This conclusion is confirmed by a comparison of the trinitroanisidines, which, by the kindness of M. Reverdin, who has sent us a specimen of his preparation, we have been enabled to make. Our acetyl derivative is easily hydrolysed by heating with excess of concentrated sulphuric acid for a few minutes to about 105° . The solution, when cold, is poured into water, and the trinitroanisidine allowed to separate. After crystallisation from alcohol it consists of dull red, glistening scales, melting at $138-139^{\circ}$:

0.0632 gave 12 c.c. N_2 (moist) at 14.7° and 747.8 mm. $N=21.90$.

$C_7H_6O_7N_4$ requires $N=21.71$ per cent.

M. Reverdin's trinitroanisidine melts at 127° . The products of diazotisation of the new trinitroanisidine will be of special interest, and we propose extending the research in this direction.

We have much pleasure, in conclusion, in expressing our thanks to Mr. Arthur S. Wilson, who has rendered us much assistance in the course of the work.

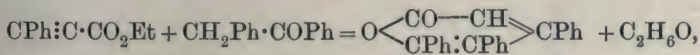
CITY AND GUILDS TECHNICAL COLLEGE, FINSBURY.

XLIX.—*Triphenyl-2-pyrone.*

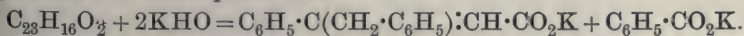
By SIEGFRIED RUHEMANN.

AFTER having found that, in the presence of sodium ethoxide, ethyl phenylpropiolate condenses with β -ketonic esters or β -diketones to 2-pyrone derivatives (Trans., 1899, **75**, 245, 411), and that the ester reacts with acetone or acetophenone to yield 4-pyrone compounds (Trans., 1908, **93**, 431, 1281), I have, for various reasons, thought fit to extend this research. In the first place, it was necessary to examine whether the formation of 4-pyrone derivatives generally takes place by the action of the acetylenic ester on ketones with the grouping $\cdot\text{CH}_2\cdot\text{CO}$. This inquiry led to the result that, so far as my observations go, this reaction is limited to those two cases, for *p*-tolyl methyl ketone, propiophenone, or methyl ethyl ketone do not condense with ethyl phenylpropiolate; the only change which occurs, is the transformation of the ester into the corresponding acid. As previously stated (*loc. cit.*), this hydrolysis takes place to some extent, also, on using acetone or acetophenone instead of the above-named ketones, and accompanies the formation of the 4-pyrone derivatives.

The behaviour of ethyl phenylpropiolate towards deoxybenzoin is different. I have undertaken this investigation in connexion with the further study on the diketopyrrolines, the results of which will be published at a later date. In the light of the work on deoxybenzoin carried out by Victor Meyer and other chemists, it was to be expected that ethyl phenylpropiolate would react with the ketone, not as it does with acetone or acetophenone, but in the manner similar to the behaviour of the acetylenic ester towards β -ketonic esters or β -diketones, thus:

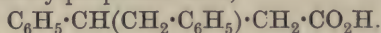


and yield 4:5:6-triphenyl-2-pyrone. This reaction does, indeed, take place. I have subjected this compound to a closer study with the view of ascertaining whether, under the influence of potassium hydroxide, it decomposes thus:



I find that only part of the pyrone compound breaks up in this way to form β -benzylcinnamic acid, melting at 168—169°. The formation of this acid is of some interest for the following reason. Whereas the homologues of cinnamic acid with the formula $\text{C}_6\text{H}_5\cdot\text{CH}:\text{CR}\cdot\text{CO}_2\text{Et}$ are readily produced according to Perkin's

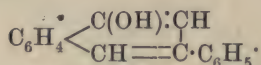
reaction, it is only recently that Schroeter (*Ber.*, 1904, **37**, 1090; 1907, **40**, 1589; 1908, **41**, 5) was able to obtain β -alkylcinnamic acids from the products of the action of zinc or magnesium on the mixture of aromatic ketones and ethyl iodoacetate (see, also, Rupe and Busolt, *Ber.*, 1907, **40**, 4537). Like Michael and Palmer's (*Amer. Chem. J.*, 1885, **7**, 69) α -benzylcinnamic acid, which on reduction yields dibenzylacetic acid, $(C_6H_5 \cdot CH_2)_2 \cdot CH \cdot CO_2H$, β -benzylcinnamic acid, on treatment with sodium amalgam, is transformed into β -phenyl- β -benzylpropionic acid,



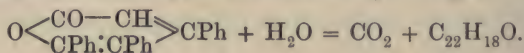
Again, just as α -benzylcinnamic acid, under the influence of cold concentrated sulphuric acid, condenses to form benzylidene-

α -hydrindone, $C_6H_4 \langle \begin{smallmatrix} CH_2 \\ CO \end{smallmatrix} \rangle C : CH \cdot C_6H_5$ (see Schmid, *J. pr.*

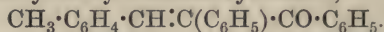
Chem., 1900, [ii], **62**, 550), β -benzylcinnamic acid is transformed into 3-phenyl-1-naphthol:



The formation of β -benzylcinnamic acid (m. p. 168—169°) is accompanied by the production of an isomeride melting between 76° and 90°, which, as yet, I have failed to obtain with a fixed melting point. But the action of potassium hydroxide on triphenyl-2-pyrone is still more complicated, because part of the pyrone compound undergoes the following change:



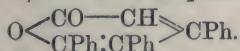
The fact that the product $C_{22}H_{18}O$, which is formed, does not melt sharply, indicates that it is a mixture, and leads to the view that the compound $CH_2 : C(C_6H_5) \cdot CH(C_6H_5) \cdot CO \cdot C_6H_5$, which may be expected to be first produced, under the influence of the alkali, is partly or wholly transformed into a mixture of stereoisomerides of phenylethylidenedeoxybenzoin, $CH_3 \cdot C(C_6H_5) : C(C_6H_5) \cdot CO \cdot C_6H_5$. All attempts to separate this mixture by crystallisation have been unsuccessful. Compounds which belong to the same type are known already. These are the alkylidenedeoxybenzoins which Klages and Tetzner (*Ber.*, 1902, **35**, 3965) prepared from deoxybenzoin. Isomeric with the product $C_{22}H_{18}O$, which is formed from triphenyl-2-pyrone, is *p*-methylbenzylidenedeoxybenzoin,



This substance was obtained by those chemists on condensing deoxybenzoin with *p*-tolualdehyde, and was found to exist in two forms, which could be separated.

EXPERIMENTAL.

Formation of 4:5:6-Triphenyl-2-pyrone,



This substance is formed on adding deoxybenzoin (9·8 grams) to dry sodium ethoxide (3·4 grams) suspended in absolute ether, and then ethyl phenylpropiolate (8·7 grams) to the solution which is shortly produced. The mixture becomes red, and a yellow solid separates. The reaction is complete in the course of a day; water is then added, when part of the solid (8 grams) remains undissolved. This is insoluble in water or alcohol; it dissolves sparingly in cold, moderately in boiling, glacial acetic acid, and, on cooling, crystallises in faintly yellow prisms, which melt at 245—246°:

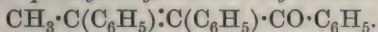
0·2030 gave 0·6342 CO₂ and 0·0930 H₂O. C=85·20; H=5·09.

C₂₃H₁₆O₂ requires C=85·18; H=4·94 per cent.

The yield of this substance is only 50 per cent. of the theoretical; this is due to the fact that part of the ethyl phenylpropiolate is transformed into the acid, which, together with the unattacked deoxybenzoin, is contained in the ethereal layer from the product of the reaction.

Action of Potassium Hydroxide on Triphenyl-2-pyrone.

On boiling the pyrone with an excess of alcoholic potassium hydroxide on the water-bath, it dissolves, yielding a deep red solution, and finally a yellow solid. After four to five hours' heating, the alcohol is distilled off, water added to the residue, and the whole extracted with ether. On evaporation of the ether, a yellowish-red oil is left behind, which gradually sets almost completely, to a solid. This is washed with a little dilute alcohol, when it becomes quite white. This product is a mixture of the stereoisomerides of *phenylethylidenedeoxybenzoin*,



It readily dissolves in hot alcohol, and, on cooling, crystallises in colourless prisms, which begin to soften at 76°, and are completely melted at 90°:

0·1882 gave 0·6110 CO₂ and 0·1090 H₂O. C=88·54; H=6·13.

0·1970 „ 0·6400 CO₂ „ 0·1080 H₂O. C=88·60; H=6·09.

C₂₂H₁₈O requires C=88·59; H=6·04 per cent.

The substance is very soluble in carbon disulphide, and moderately so in light petroleum; it dissolves slowly in cold concentrated sulphuric acid, forming a red solution. I have repeatedly crystallised

the product from alcohol as well as from light petroleum, but all the fractions, on melting, showed practically the same behaviour, and, on analysis, gave the same results.

The alkaline solution from the product of the action of potassium hydroxide on the pyrone, which contains a mixture of benzoic acid and the isomeric β -benzylcinnamic acids, is mixed with an excess of dilute sulphuric acid and repeatedly extracted with ether. On evaporation of the ether, a yellow oil is left behind, which sets to a solid after a few hours. When this is washed with cold dilute alcohol, β -benzylcinnamic acid remains undissolved.

β -Benzylcinnamic Acid, $C_6H_5 \cdot C(CH_2 \cdot C_6H_5) : CH \cdot CO_2H$.

The acid is only sparingly soluble in cold alcohol, but readily so in boiling alcohol, and, on cooling, separates in long, colourless needles, which melt at $168-169^\circ$:

0.2028 gave 0.5992 CO_2 and 0.1080 H_2O . $C=80.58$; $H=5.92$.

$C_{16}H_{14}O_2$ requires $C=80.64$; $H=5.88$ per cent.

β -Benzylcinnamic acid is readily soluble in ammonia, and this solution, on the addition of silver nitrate, yields a white silver salt, which is sparingly soluble in boiling water:

0.2595 gave 0.0810 Ag. $Ag=31.21$.

$C_{16}H_{13}O_2Ag$ requires $Ag=31.30$ per cent.

β -Phenyl- β -benzylpropionic Acid, $C_6H_5 \cdot CH(CH_2 \cdot C_6H_5) \cdot CH_2 \cdot CO_2H$.

The reduction of β -benzylcinnamic acid readily takes place on dissolving it in dilute sodium hydroxide and shaking the solution with an excess of sodium amalgam ($2\frac{1}{2}$ per cent.) for about half an hour. The alkaline liquor is poured off and mixed with dilute hydrochloric acid, when an oil separates which solidifies in the course of a day. The solid is sparingly soluble in light petroleum, readily so in chloroform or alcohol; on adding water to the hot alcoholic solution until it becomes turbid, colourless prisms gradually separate, which melt at $95-96^\circ$:

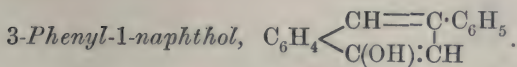
0.1978 gave 0.5810 CO_2 and 0.1190 H_2O . $C=80.10$; $H=6.71$.

$C_{16}H_{16}O_2$ requires $C=80.0$; $H=6.67$ per cent.

The silver salt, which is formed on the addition of silver nitrate to the ammoniacal solution of the acid, is white, and does not change on drying in the water-oven:

0.2438 gave 0.0758 Ag. $Ag=31.09$.

$C_{16}H_{15}O_2Ag$ requires $Ag=31.12$ per cent.



On adding cold concentrated sulphuric acid to β -benzylcinnamic acid, the crystals gradually dissolve, forming a red solution which, when kept overnight and then slowly poured into cold water, yields an oil. This gradually sets to a solid, which is sparingly soluble in boiling water, readily so in ether, chloroform, or alcohol; it is purified by adding water to the alcoholic solution until an emulsion is produced, from which light brown needles, melting at $100\text{--}101^\circ$, separate:

0.1883 gave 0.6023 CO_2 and 0.0950 H_2O . $\text{C}=87.23$; $\text{H}=5.60$.

$\text{C}_{16}\text{H}_{12}\text{O}$ requires $\text{C}=87.27$; $\text{H}=5.45$ per cent.

This compound is very soluble in alkalis, and does not give a colour reaction on the addition of ferric chloride to its alcoholic solution.

The alkaline solution, which is formed by the action of potassium hydroxide on triphenyl-2-pyrone, contains, besides β -benzylcinnamic acid, melting at $168\text{--}169^\circ$, its isomeride. This, being very soluble in alcohol, remains in the original alcoholic filtrate from the former acid, together with benzoic acid, which, also, is produced in the reaction. In order to remove the benzoic acid, water is added to the filtrate, and the whole extracted with ether. The product which is left behind on evaporation of the ether is distilled in a current of steam, the benzoic acid contained in the distillate is extracted with ether, and, after evaporation of the ether, re-crystallised from water. The isomeride of β -benzylcinnamic acid is not volatile with steam, and remains in the distilling flask as an oil, which slowly solidifies. The solid is very soluble in alcohol, ether, warm carbon disulphide, or chloroform, sparingly so in light petroleum. The solution in the latter solvent gradually deposits stout prisms, which soften at 104° , and are completely melted at 116° . That this substance is isomeric with β -benzylcinnamic acid, melting at 168° , is proved by the following analysis:

0.1900 gave 0.5620 CO_2 and 0.1023 H_2O . $\text{C}=80.67$; $\text{H}=5.98$.

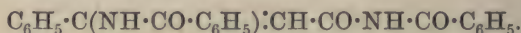
$\text{C}_{16}\text{H}_{14}\text{O}_2$ requires $\text{C}=80.64$; $\text{H}=5.88$ per cent.

The fact that this substance does not fuse sharply seems to indicate that it is not pure, but after repeated crystallisations from dilute alcohol or light petroleum, the behaviour on melting is practically unaltered.

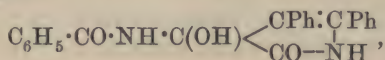
L.—*Diketodiphenylpyrroline and its Analogues.*
Part III.

By SIEGFRIED RUHEMANN.

THE formation of the diketodiphenylpyrrolines by the action of ethyl phenylpropiolate on the sodium derivatives of aromatic amides is accompanied by the production of colourless compounds (see Ruhemann, *Trans.*, 1909, **95**, 984, 1603). One of these substances had been isolated previously (*loc. cit.*) from the product of the reaction of sodiobenzamide with the acetylenic ester, and its formula was found to be $C_{23}H_{18}O_3N_2$. With regard to its constitution, the view was expressed that this substance was the result of the union of benzamide with the first formed phenylpropiolylbenzamide, and that, accordingly, it was represented thus:



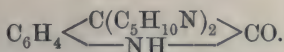
A closer investigation, however, did not confirm this view; for the colourless substance, $C_{23}H_{18}O_3N_2$, on boiling with potassium hydroxide decomposes to yield deoxybenzoin, and with cold concentrated sulphuric acid breaks up quantitatively into diketodiphenylpyrroline and benzamide. This behaviour, and the fact that the compound has no basic properties, lead to the conclusion that it is to be regarded as an additive product of diketodiphenylpyrroline with benzamide. Its constitution, therefore, is to be expressed thus:



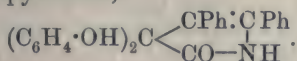
and it is therefore 3-benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline.

This result induced me to examine whether the diketopyrroline forms additive products with other substances, and in this respect, also, resembles isatin. It was found, indeed, that, like the latter compound (see Baumann, *Ber.*, 1885, **18**, 890), the diketopyrroline readily unites with phenylmercaptan to yield an additive compound, $C_{16}H_{11}O_2N, C_6H_6S$, which undoubtedly has a constitution similar to the additive product with benzamide, and which readily decomposes into its constituents, phenylmercaptan and the diketopyrroline. With piperidine, the diketopyrroline combines even in the cold to form the compound $C_{16}H_{11}O_2N, C_5H_{11}N$. This is more stable than the former substance, and does not decompose until its solutions in mineral acids are heated, when the diketopyrroline separates. The behaviour of piperidine towards isatin was examined

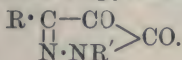
by Schotten (*Ber.*, 1891, **24**, 1367), who carried out the reaction at the temperature of the water-bath, and thus obtained dipiperidylisatin,



The resemblance between isatin and the diketopyrrolines is further indicated by the fact that they give the indophenine reaction. On shaking their solutions in concentrated sulphuric acid with benzene which contains thiophen, the red colour first changes to brown, and then gradually turns blue. Like isatin, diketodiphenylpyrroline condenses with phenol in the presence of concentrated sulphuric acid, and forms 2-keto-3:3-bishydroxyphenyl-4:5-diphenylpyrroline,



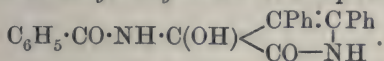
It may finally be stated that the relation which isatin exhibits to the diketopyrrolines as well as to the diketo-derivatives of *cyclopentene* extends also to the diketopyrazolines:



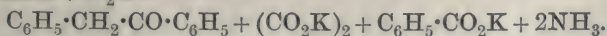
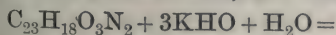
One member of this class of compounds, namely, 4:5-diketo-1-phenyl-3-methylpyrazoline, was first prepared by Knorr and Pschorr (*Annalen*, 1887, **238**, 194); afterwards Sachs and Barschall (*Ber.*, 1902, **35**, 1437; 1903, **36**, 1132) obtained diketopyrazolines by the action of nitrosodimethylaniline on the pyrazolones and subsequent treatment of the former condensation products with mineral acids. Up to the present, however, no member of this group of diketo-compounds is known in which the iminic hydrogen of the pyrazoline ring is intact. I propose to prepare such substances with the view of ascertaining whether they behave towards alkalis like their analogues and form blue salts.

EXPERIMENTAL.

3-Benzoylamino-3-hydroxy-2-keto-4:5-diphenylpyrroline,



On boiling this compound with an excess of concentrated potassium hydroxide, it decomposes and yields ammonia, deoxybenzoin, oxalic acid, and benzoic acid, thus:



The heating was continued until ammonia ceased to be evolved;

steam was then passed through the product of the reaction, when a solid slowly passed over which, after crystallisation from light petroleum, melted at 60—61°. This substance was deoxybenzoin:

0.1732 gave 0.5440 CO₂ and 0.0962 H₂O. C=85.66; H=6.17.

C₁₄H₁₂O requires C=85.71; H=6.12 per cent.

The remaining alkaline solution was treated with an excess of dilute sulphuric acid and subjected to steam distillation. The benzoic acid which is contained in the distillate was extracted with ether, recrystallised from water, and identified by the melting point. The formation of oxalic acid in the reaction was ascertained by the usual test.

The result of the action of potassium hydroxide on the colourless substance C₂₃H₁₈O₃N₂ indicates that it is an additive product of diketodiphenylpyrrolin_e with benzamide, and this conclusion is supported by the fact that, with sulphuric acid, the substance breaks up into these components. On adding the colourless compound to the concentrated acid, it dissolved, yielding a deep red solution. This, after being kept overnight, was gradually poured into cold water, and the diketodiphenylpyrroline, which separated, was crystallised from dilute alcohol. It softens at 184°, and melts at 190—191° (instead of 184°, which was previously given as the melting point):

0.1948 gave 0.5505 CO₂ and 0.0820 H₂O. C=77.07; H=4.67.

C₁₆H₁₁O₂N requires C=77.11; H=4.42 per cent.

The benzamide which is contained in the filtrate from the diketopyrroline was extracted with ether, and, on evaporation of the ether, remained as a red solid, which, after crystallisation from water, melted at 130°:

0.2338 gave 24.2 c.c. N₂ at 18° and 754 mm. N=11.84.

C₇H₇ON requires N=11.57 per cent.

Additive Product of Diketodiphenylpyrroline and Phenylmercaptan,
C₁₆H₁₁O₂N, C₆H₆S.

This additive product is readily formed on adding phenylmercaptan to the diketopyrroline, dissolved in hot alcohol. The deep colour of the solution turns light red, and faintly pink plates soon separate. These were washed with ether and dried in a vacuum desiccator over sulphuric acid. The substance reddens at about 140°, and melts at 174—175°:

0.1760 gave 0.4755 CO₂ and 0.0785 H₂O. C=73.68; H=4.96.

0.2240 „ 0.1476 BaSO₄; S=9.05.

C₂₂H₂₇O₂NS requires C=73.53; H=4.74; S=8.91 per cent.

On adding this compound to cold concentrated sulphuric acid,

heat is developed, the odour of phenylmercaptan is perceptible, and a deep red solution is produced, which yields a precipitate of diketodiphenylpyrroline when poured into water.

Additive Product of Diketodiphenylpyrroline and Piperidine,
 $C_{16}H_{11}O_2N, C_5H_{11}N$.

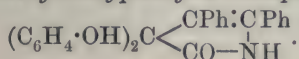
On adding piperidine to the diketopyrroline dissolved in ether, the red colour of the solution changes to yellow, and, after a short time, faintly brown, glistening prisms separate, which melt and decompose at $180-181^\circ$:

0.1632 gave 12.2 c.c. N_2 at 20° and 749 mm. $N=8.42$.

$C_{21}H_{22}O_2N_2$ requires $N=8.38$ per cent.

The substance is rather stable towards mineral acids; decomposition into its constituents, the diketopyrroline and piperidine, does not take place until the solutions are heated.

2-Keto-3: 3-bishydroxyphenyl-4: 5-diphenylpyrroline,



Phenol reacts with diketodiphenylpyrroline under the same conditions as with isatin (see von Baeyer and Lazarus, *Ber.*, 1885, **18**, 2641). The diketopyrroline (2 grams) was dissolved in an excess of phenol, and, gradually, concentrated sulphuric acid was added until the red colour of the solution turned deep brown. The whole was then poured into water, when a yellow, flocculent solid was precipitated. This was dissolved in ether, and the solution mixed with chloroform until it became turbid. In the course of a few hours, yellow plates separated, which retained their colour even on boiling the alcoholic solution with animal charcoal. The substance melts at $220-221^\circ$:

0.1600 gave 0.4697 CO_2 and 0.0755 H_2O . $C=80.06$; $H=5.24$.

0.2420 „ 7.2 c.c. N_2 at 17° and 747 mm. $N=3.39$.

$C_{28}H_{21}O_3N$ requires $C=80.19$; $H=5.01$; $N=3.34$ per cent.

This compound is sparingly soluble in chloroform or benzene, moderately so in ether or cold alcohol, but readily so in boiling alcohol. It dissolves in potassium hydroxide, yielding a yellow solution, from which it is precipitated unchanged on the addition of hydrochloric acid.

LI.—*The Constitution of Carpaine. Part I.*

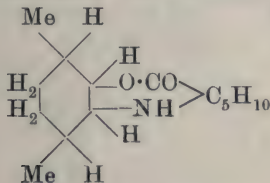
By GEORGE BARGER.

THE alkaloid carpaine was discovered by Greshoff in the leaves of the Papaw tree, *Carica Papaya*, L. (*Mededeelingen uit 's Lands Plantentuin*, No. 7, Batavia, 1890, p. 5). Merck (*Jahresber.*, 1891, p. 30) assigned to it the formula $C_{14}H_{27}O_2N$, but van Ryn (*Inaug. Diss. Marburg*, 1892; *Arch. Pharm.*, 1893, **231**, 184; 1897, **235**, 332) corrected this to $C_{14}H_{25}O_2N$. Van Ryn described a number of salts, and showed that carpaine is a secondary base yielding a nitroso-derivative, $C_{14}H_{24}O_2N \cdot NO$, and that on methylation and ethylation a tertiary base and quaternary iodide are produced. He also attempted to obtain a knowledge of the constitution by oxidation with potassium permanganate, but his experiments in this direction were unsuccessful.

The alkaloid for the present investigation was prepared from Papaw leaves from British India; the yield was 0.07 per cent., or the same as that obtained by Greshoff from adult leaves (young leaves contain three to four times as much).

The experimental results which have been obtained so far show that carpaine is the internal anhydride of a substance possessing both acid and basic properties, and closely resembling certain amino-acids; this substance contains a carboxyl group, and has the composition $C_{14}H_{27}O_3N$; the name *carpamic acid* is suggested for it. By oxidation with potassium permanganate, or preferably with nitric acid, a dibasic acid of the composition $C_8H_{14}O_4$ is formed, which is probably $\alpha\delta$ -dimethyladipic acid; this acid might result from the breaking down of a dimethylcyclohexane ring. Like carpaine itself, the ethyl ester of carpamic acid yields a nitroso-derivative, whence it follows that the alkaloid cannot be a lactam, but must be a lactone, and that its two oxygen atoms are arranged as follows: $:C \cdot O \cdot CO \cdot$. Although there is at present no direct evidence, it thus appears very probable that carpamic acid contains an alcoholic hydroxyl in addition to a carboxyl group and an imino-group; if attached to the cyclohexane ring, this hydroxyl would be converted on oxidation into one of the carboxyl groups of the acid $C_8H_{14}O_4$. In this case the carboxyl group of carpamic acid could not be directly connected to the cyclohexane ring, but would be attached to the rest of the molecule. The oxidation of carpaine by potassium permanganate (see below) affords some evidence that the nitrogen atom is directly attached to the complex yielding the acid $C_8H_{14}O_4$; the rest of the molecule left unaccounted for is a bivalent group,

C_5H_{10} . The subjoined largely hypothetical formula will serve to



show that if carpaine contains 25 hydrogen atoms, there can only be one homocyclic ring, in addition to the lactone ring. With regard to the complex C_5H_{10} , nothing is known at present.

EXPERIMENTAL.

Composition and Properties of Carpaine.

Van Ryn's analyses agree closely with the formula $C_{14}H_{25}O_2N$, and so far it was thought unnecessary to confirm this. It is, however, supported indirectly by the analyses of carpamic acid and its derivatives. Merck's formula, $C_{14}H_{27}O_2N$, is certainly incorrect, and the only other formula, $C_{14}H_{23}O_2N$, is hardly more likely.

The properties of carpaine have been fully described by van Ryn, except the fact that the alkaloid can be distilled without decomposition. In a vacuum produced by charcoal and liquid air (the pressure was a fraction of a millimetre), 2 grams of carpaine were distilled with the bath at $260-290^\circ$, and the vapour at $215-235^\circ$. The distillate crystallised in the receiver, and at once showed the melting point 121° (corr.), identical with that given by van Ryn.

Action of Acids on Carpaine: Carpamic Acid.

Van Ryn attempted to hydrolyse carpaine by boiling it with 1 per cent. alcoholic hydrogen chloride, but after twelve hours almost the whole of the alkaloid was recovered unchanged. This acid was much too dilute, and the temperature too low. When heated in a sealed tube to $130-140^\circ$ for a few hours with 10 per cent. hydrochloric or sulphuric acid, carpaine is quantitatively changed to a substance containing one molecule of water more than carpaine. The same change may be brought about more slowly by boiling with 20 per cent. hydrochloric acid. The completion of the change is best detected by the disappearance of the intensely bitter taste of carpaine. When sulphuric acid has been used it may be removed with baryta, which does not precipitate the product of hydrolysis; in the case of hydrochloric acid, the excess of the acid can be removed by distillation under diminished pressure. The

hydrochloride of carpamic acid remains behind as a syrup, and crystallises on cooling. It may be recrystallised from acetone, or by adding ether to its alcoholic solution, and forms needles melting at 161° :

0.1320 gave 0.2778 CO_2 and 0.1107 H_2O . $\text{C}=57.4$; $\text{H}=9.3$.

0.1270 „ 0.0627 AgCl . $\text{Cl}=12.2$.

$\text{C}_{14}\text{H}_{27}\text{O}_3\text{N}, \text{HCl}$ requires $\text{C}=57.2$; $\text{H}=9.5$; $\text{Cl}=12.1$ per cent.

The free base may be obtained from the hydrochloride by decomposition with the calculated quantity of sodium carbonate, but as the substance is readily soluble in water and scarcely more soluble in alcohol than sodium chloride, it is difficult to obtain it quite free from salt by this means. It is therefore better to decompose the sulphate with baryta, or the hydrochloride with moist silver oxide, and to crystallise the residue left on evaporating the aqueous filtrate from dilute alcohol. It also crystallises very well on adding acetone to the cold alcoholic solution.

Carpamic acid, obtained in this manner, forms long needles, melting at 224° . Under a pressure of less than 1 mm., the substance sublimes unchanged; when heated under atmospheric pressure, it distils with slight decomposition:

0.1212 gave 0.2925 CO_2 and 0.1139 H_2O . $\text{C}=65.8$; $\text{H}=10.4$.

$\text{C}_{14}\text{H}_{27}\text{O}_3\text{N}$ requires $\text{C}=65.4$; $\text{H}=10.5$ per cent.

The substance is optically active; in aqueous solution:

$l=1\text{-dcm.}$; $c=3.727$; $\alpha_D + 0.26^{\circ}$; $[\alpha]_D + 7.0^{\circ}$.

Carpamic acid is readily soluble in cold water, but only very sparingly so in alcohol; it is insoluble in acetone, ether, and most other organic solvents. The salts with mineral acids and with the alkali metals are readily soluble in water; the barium salt is a stiff jelly, so that the test-tube in which it is formed can be inverted. Carpamic acid has a hardly perceptible, faintly sweet taste, like some amino-acids; when pure and free from carpaine, the intense bitter taste of the latter alkaloid is absent. In dilute solution carpamic acid does not yield precipitates with potassium tri-iodide or with potassium mercuri-iodide, differing therein from carpaine; both bases, however, yield a precipitate with phosphomolybdic acid.

In solubilities, volatility, and chemical reactions, carpamic acid closely resembles certain amino-acids like leucine, but it has more definitely basic properties than are associated with α -amino-acids. The presence of a carboxyl group is demonstrated by esterification. Thus, when carpamic acid is suspended in absolute alcohol and treated with hydrogen chloride, there remains on evaporation of the acid a syrup, which crystallises on the addition of ether to its

concentrated alcoholic solution, forming needles, melting at 171—172°, and consisting of the *hydrochloride of ethyl carpamate*:

0.1354 gave 0.2968 CO₂ and 0.1178 H₂O. C=59.8; H=9.7.

C₁₆H₃₁O₃N.HCl requires C=59.7; H=9.9 per cent.

The same hydrochloride is formed almost quantitatively direct from carpaine by hydrolysis with alcoholic (instead of with aqueous) hydrochloric acid. For instance, 0.5 gram of carpaine, heated with 5 c.c. of 10 per cent. alcoholic hydrogen chloride for two hours to 160°, yielded 0.51 gram of this hydrochloride on addition of ether to its concentrated alcoholic solution.

The hydrochloride of ethyl carpamate is tasteless; its aqueous solution is precipitated by sodium carbonate. The free ester base is readily soluble in ether; it has not yet been crystallised.

From the above description it will be seen that carpaine and carpamic acid are related to each other in the same way as ergotinine and ergotoxine (Barger and Ewins, this vol., p. 284). Both carpaine and ergotinine are converted by acids in alcoholic solution into salts of an ester.

Action of Alkalis on Carpaine.

Carpaine is extremely resistant to alkalis. Thus, after 0.2 gram had been heated with 2 c.c. of 10 per cent. aqueous sodium hydroxide to 140—150° for three and a-half hours, 0.16 gram of carpaine was recovered unchanged. The carpaine was hardly attacked, because it is insoluble in water. In a similar experiment with 2 c.c. of 2.5*N*-sodium ethoxide, carpamic acid was formed, and when 0.2 gram had been heated to 180° for two hours with 4 c.c. of 3.3*N*-sodium ethoxide, 0.12 gram of carpamic acid was obtained.

On fusion with alkali, a further change may take place. When 0.5 gram of carpaine was heated with 7 grams of potassium hydroxide and 0.5 c.c. of water, no apparent change took place below 300°. Then a dark brown solution was gradually formed, and, on cooling, hydrochloric acid yielded an oily precipitate soluble in ether with intense fluorescence. On evaporation, the ether left a red oil, which with ferric chloride yielded a reddish-brown coloration. It would appear that under these conditions a phenol is formed (by oxidation of a *cyclohexane* ring); a similar product was also obtained on chlorinating carpaine and treating the product with alkali (see below).

Further Degradation of Carpamic Acid.

This cannot readily be brought about by boiling with alkali. In one experiment 0.2 gram of carpaic acid was boiled with 6 c.c. of

50 per cent. potassium hydroxide solution. The potassium salt of the acid floated on top as a brown oil, and during half an hour's boiling very little, if any, of a volatile base was given off, corresponding at most to one-fiftieth of the nitrogen present. On cooling, the upper layer crystallised; it yielded, on acidification, unchanged carpamic acid.

By distilling carpamic acid with lime under diminished pressure, a little of an oily base is formed, insoluble in water, but soluble in ether. A similar base is formed on heating carpamic acid (or carpaine) with concentrated hydrochloric acid to 225—250°. In both cases the carboxyl group of carpamic acid seems to be eliminated, but neither reaction has been studied further for want of material.

Oxidation of Carpaine.

Carpaine is fairly resistant to oxidising agents. Van Ryn found that acid potassium permanganate is only very slowly decolorised at room temperature. By heating on the water-bath (in dilute sulphuric acid solution), oxidation was more rapid, and he obtained a mixture of crystalline, non-nitrogenous acids, the yield of which was, however, only 7½ per cent. of the alkaloid employed. By crystallisation from water, three fractions were obtained, melting continuously from 70—124°; the small yield of material available did not enable van Ryn to isolate any of the acids in a state of purity, and no analysis was made. The only other product obtained was ammonia.

In view of the difficulties encountered by van Ryn, it was thought advisable to modify the conditions of oxidation by using neutral potassium permanganate in acetone solution, a method which has of late yielded such good results in the case of brucine and strychnine (Leuchs, *Ber.*, 1908, **41**, 1711). Five grams of carpaine were dissolved in 125 c.c. of acetone, and 1.11 grams of finely powdered potassium permanganate (half an atomic proportion of oxygen) was added to the solution after cooling to 0°. The pink colour disappeared only very slowly. The solution was therefore warmed to room temperature, when the permanganate was completely reduced in a few hours. The same quantity was then again added; finally, when two atoms of oxygen had been used up, the solution was filtered, and was found to contain 2½—3 grams of the unchanged alkaloid.

In a second experiment 5 grams of carpaine in 140 c.c. of acetone were at once treated with 3.33 grams of potassium permanganate (=1½ atoms of oxygen); the temperature gradually rose from 23° to 37°, and then fell; the pink colour disappeared in half an hour. In all, 9 atoms of oxygen were supplied; the addition of per-

manganate, representing the last atom of oxygen, produced a rise of temperature only from 21—25°, and this time the pink colour persisted after seven hours. On filtration, the acetone was found to contain only a minute quantity of a neutral substance, melting at about 50°. The mixture of manganese dioxide and potassium salts was extracted with water (by shaking, glass beads being added). The pale brown solution was washed with ether, which did not remove an appreciable amount of substance; the solution was then acidified and became turbid; by repeated extracting with ether, 2.5 grams of a brown syrup were now obtained, but the aqueous solution still held in suspension a considerable quantity of a brown, oily substance, which was almost insoluble in ether. The syrup extracted by ether was esterified with methyl alcohol and hydrogen chloride, and was then distilled; between 110—120° at a pressure of 3—4 mm., there was collected a small quantity of a distillate, which was hydrolysed by boiling with potassium hydroxide; at the same time an alkaline gas (ammonia or an amine) was evolved. On acidification, 0.15 gram of an acid was obtained, which, on crystallisation from benzene, formed leaflets, melting not quite sharply at 98—100°. This acid was free from nitrogen, and was analysed:

0.0682 gave 0.1398 CO₂ and 0.0496 H₂O. C=55.9; H=8.1.

[C₈H₁₂O₄ requires C=55.8; H=7.0 per cent.]

C₈H₁₄O₄ „ C=55.2; H=8.0 „

The molecular weight was determined by the author's microscopic method (Trans., 1904, 85, 286):

0.0487, in 1.2744 grams methyl alcohol, was intermediate between 0.20 and 0.21 mol. benzil. M.W.=182—191, mean 186.

C₈H₁₄O₄ requires M.W.=174.

0.0164 gram of acid required for neutralisation 1.62 c.c. N/10-KOH, whence M.W. for a dibasic acid=204.

In the distillation of the ester a small quantity of a semi-solid fraction was further collected, boiling at 120—200°/3 mm., but the bulk of the material decomposed in the flask. It thus became evident that much more than 5 grams of the alkaloid would be required for the complete characterisation of the acid (van Ryn obtained no result from the oxidation of 10 grams with potassium permanganate). Other oxidising agents were therefore employed, and among these nitric acid was found to be much the most suitable. 0.2 Gram of carpaine, heated in a sealed tube with 2 c.c. of nitric acid (D 1.41) to 140—170°, yielded only a minute quantity of an acid soluble in water, which on heating gave an odour similar to that of succinic anhydride; there was no trace of

an alkaloidal substance. On opening the tube there was great pressure, most of the alkaloid having been oxidised to carbon dioxide. In a similar experiment with acid of density 1.32, 40 per cent. of a dibasic acid was obtained, and after a large number of such experiments the exact conditions were found for obtaining a mixture of non-nitrogenous acids weighing 75 per cent. of the alkaloid employed. This mixture is at present under investigation, and from it an acid of the composition $C_8H_{14}O_4$ has been isolated, which is probably a mixture of the two stereoisomeric forms of $\alpha\delta$ -dimethyladipic acid, the same mixture having previously been obtained in very much smaller amount with potassium permanganate.

The oxidation of carpaine by halogens was also attempted. When chlorine is passed into a cold aqueous solution of the hydrochloride, the whole of the alkaloid is gradually precipitated as an amorphous chloro-derivative, which is decomposed by boiling alcohol, but can be crystallised from methyl alcohol (with considerable loss), forming leaflets, melting and decomposing at 77° :

0.0981 * gave 0.1854 CO_2 and 0.0618 H_2O . $C=51.7$; $H=7.0$.

0.1247 † „ 0.1132 AgCl. $Cl=22.5$.

$C_{14}H_{23}O_3NCl_2$ requires $C=51.8$; $H=7.1$; $Cl=21.9$.

This substance is neutral; two hydrogen atoms have been replaced by an oxygen atom and two chlorine atoms; it is therefore dichloro-oxycarpaine, and as it is formed quantitatively, it was thought that it might form a suitable starting point for further degradation. The chlorine is very readily removed, by cold pyridine, for instance, but the substance is not simply a perchloride. A somewhat profound change has taken place; carpaine cannot be recovered from it, and by treatment with alkali a pink, fluorescent solution is obtained (benzene derivative?). So far it has been found impossible to obtain any further derivative in a pure state.

On passing chlorine into a solution of carpamic acid, a similar derivative is formed, which could not, however, be crystallised.

Bromine produces in a solution of a carpaine salt an orange precipitate of a perbromide, from which carpaine is readily regenerated.

In comparing the oxidation by potassium permanganate in acetone solution with that by nitric acid at 130° , it should be noted that the latter reagent first hydrolyses the alkaloid to carpamic acid, which thus becomes open to attack. A non-nitrogenous acid is then formed, but potassium permanganate first produces a nitrogenous acid, which is only slightly soluble in ether. After dis-

* Crystallised.

† Amorphous, dried in a vacuum.

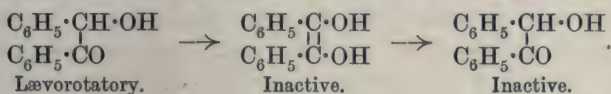
tillation the ester of this acid gave off an amine or ammonia on hydrolysis, the same acid, $C_8H_{14}O_4$, resulting. From this it would appear that the nitrogen atom is directly attached to the complex yielding this acid.

THE GOLDSMITHS' COLLEGE,
NEW CROSS, LONDON, S.E.

LII.—*Optically Active Glycols Derived from l-Benzoin and from Methyl l-Mandelate.*

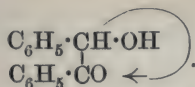
By ALEX. MCKENZIE and HENRY WREN.

THE work described in the present communication was undertaken in consequence of the racemisation phenomena which were observed by one of us (Wren, Trans., 1909, 95, 1583, 1593) in connexion with the study of *l*-benzoin and its derivatives. *l*-Benzoin, which is prepared from magnesium phenyl bromide and *l*-mandelamide (McKenzie and Wren, Trans., 1908, 93, 312), has $[\alpha]_D - 119^\circ$ in acetone solution, and undergoes complete racemisation with great readiness in the presence of alkali. The interpretation was suggested that the isomeric change in question was probably of a keto-enolic character, the hypothetical ω -dihydroxystilbene being formed as an intermediate phase:

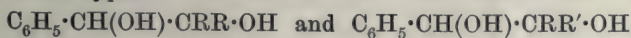


The racemisation of *l*-benzoin methyl ether also proceeds with great readiness in the presence of alkali.

In accordance with this view, the hydrogen attached to the carbon atom of the $:CH \cdot OH$ group migrates to the adjacent carbonyl-oxygen atom:



Desmotropic change of this nature is, however, impossible if the carbonyl group in *l*-benzoin is displaced by the $CRR \cdot OH$ group, a transformation which can be effected by the application of Grignard's reaction to *l*-benzoin. We find accordingly that optically active glycols of the types:



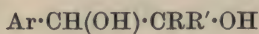
do not lose their activity in the presence of alkali. The triphenyl

glycol, obtained from methyl *l*-mandelate and magnesium phenyl bromide, has $[\alpha]_D + 221.3^\circ$ in acetone solution, and is perfectly stable even when boiled with *N*/10-alcoholic potash for thirty minutes.

Similarly, the diphenylethyl glycol, obtained from *l*-benzoin and magnesium ethyl iodide, retains its activity unchanged during twenty-five hours at the ordinary temperature when dissolved in *N*/10-alcoholic potash, whereas *l*-benzoin methyl ether, under the same conditions, is racemised completely within five minutes.

The conversion of methyl *l*-mandelate, a highly active lævoro-rotatory compound with $[\alpha]_D - 236^\circ$ in carbon disulphide solution (Wren, *loc. cit.*), into the highly active dextrorotatory triphenyl glycol, referred to above, suggested the possibility of a Walden inversion having occurred in this change. In order to obtain further evidence on this point, the action of magnesium phenyl bromide on *l*-benzoin was examined, when it was found that the resulting glycol was dextrorotatory and identical with the product from methyl *l*-mandelate. There is thus no evidence of a Walden inversion in either of these actions, and it is accordingly proposed to designate the dextrorotatory glycols, derived either from methyl *l*-mandelate or from *l*-benzoin, as *l*-compounds.

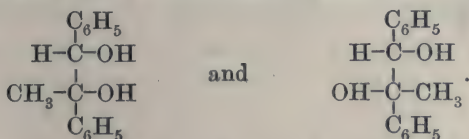
Desyl chloride has not yet been obtained in an optically active form, and we therefore treated *l*-benzoin with thionyl chloride, in the hope of obtaining an interesting compound in which the displacement of the chlorine by the hydroxy-group might be studied. Unfortunately, the product of the action was inactive desyl chloride. The displacement by the chlorine atom of the tertiary hydroxy-group in the active glycols, which are described in this paper, has not, so far, been attempted, since the action both of thionyl chloride and of fuming hydrochloric acid on inactive triphenylethylene glycol caused the elimination of one molecular proportion of water with the formation of triphenylvinyl alcohol. Now Tiffeneau (*Compt. rend.*, 1908, 146, 29) has found that the latter alcohol is also formed from triphenylethylene glycol by means of sulphuric acid; this behaviour is, however, abnormal, the researches of Tiffeneau showing that the elimination of water from the glycols of the type:



results in other cases in the formation of aldehydes of the type: $\text{ArRR}'\text{C}\cdot\text{CHO}$.

A further point arose in connexion with the interaction of *l*-benzoin and magnesium methyl iodide. Whilst the former compound contains only *one* asymmetric carbon atom, the carbon atom of the carbonyl group becomes asymmetric during this action, so that the formation

of two isomeric lævorotatory glycols, each one of which contains *two* asymmetric carbon atoms, is theoretically possible :



These glycols are not, of course, enantiomorphously related, and might be expected to be produced in unequal amounts. Only one isomeride was obtained. Again, when *r*-benzoin was acted on by magnesium methyl iodide, only one of the two possible inactive glycols was isolated, and it was obvious from the yield that the other isomeride could have been present only in small amount, or not at all.

The only glycol of the type $\text{R}\cdot\text{CH}(\text{OH})\cdot\text{CRR}\cdot\text{OH}$ known up to 1904 was the triphenylethylene glycol described by Gardeur (*Bull. Acad. roy. Belg.*, 1897, [iii], 34, 67). Acree (*Ber.*, 1904, 37, 2753) has shown that similar glycols are obtained by the aid of Grignard's action (compare also Tiffeneau and Dorlencourt, *Ann. Chim. Phys.*, 1909, [viii], 16, 237, and other papers). These compounds are all optically inactive. The Grignard action as applied to an ester of an optically active hydroxy-acid was studied for the first time by P. F. Frankland and Twiss (*Trans.*, 1904, 85, 1666), who prepared *d*-ααδδ-tetraphenylerythritol by the interaction of methyl *d*-tartrate and magnesium phenyl bromide. This ditertiary glycol is characterised by the high dextrorotation which it exhibits when contrasted with that of the tartrate from which it is derived.

In the course of the large amount of work carried out by many chemists on the connexion between unsaturated or negative groups and optical activity, the abnormal effects produced by the phenyl group have been repeatedly observed. It is, therefore, not surprising that such effects should be encountered with the compounds which are now described.

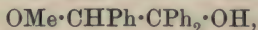
Purdie has shown that the substitution of the hydrogen atom of the alcoholic hydroxy-groups in the optically active lactic, malic, and tartaric acids (or their esters) by an alkyl group causes a very pronounced rise of optical activity. When a similar displacement is effected in *l*-mandelic acid, no such effect is observed (McKenzie, *Trans.*, 1899, 75, 753). Again, methyl *l*-mandelate,



has $[\alpha]_{\text{D}} - 236^\circ$ in carbon disulphide solution (Wren, *loc. cit.*), whereas methyl *l*-phenylmethoxyacetate, $\text{C}_6\text{H}_5\cdot\text{CH}(\text{OMe})\cdot\text{CO}_2\text{Me}$ (see experimental part) has $[\alpha]_{\text{D}} - 101.7^\circ$ in the same solvent. The com-

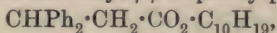
parison between the effect on rotatory power which is brought about by the displacement of the hydroxy-group in *l*-mandelic acid (or its methyl ester) by the methoxy-group, and a similar displacement in aliphatic hydroxy-acids (or esters), leads to the conclusion that the great difference between the two cases is due to the influence exerted by the phenyl group.

When *l*-triphenylethylene glycol, $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$, is alkylated by means of silver oxide and methyl iodide, only one of the two hydroxy-groups undergoes methylation. It is shown that the mono-methoxy-derivative, obtained in this manner, has the formula

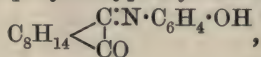


and not $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OMe}$, and that the introduction of the methyl group into the molecule of the triphenyl glycol lowers the value for the specific rotation to $+185.3^\circ$ in acetone solution.

In a recent exhaustive study of the influence of constitution on the rotatory power of optically active compounds, Rupe (*Annalen*, 1909, 369, 311; compare also *ibid.*, 1903, 327, 157) points out that the *l*-menthyl esters of saturated acids, derived from phenylcinnamic acids, possess a higher degree of optical activity than the corresponding esters of the unsaturated acids. The normal effect which Rupe observed in this particular group appears to be that negative groups lower the rotatory power in a pronounced manner. Thus, in *l*-menthyl β -phenylcinnamate, $\text{CPh}_2\cdot\text{CH}\cdot\text{CO}_2\cdot\text{C}_{10}\text{H}_{19}$, with $[\alpha]_D -37.92^\circ$ in benzene solution, the optical effect caused by the asymmetric menthyl group is influenced by the electronegative character of two phenyl groups and of one double linking. When one of these negative factors is eliminated, for instance, the double linking, the rotatory power is enhanced, thus *l*-menthyl $\beta\beta$ -diphenylpropionate,



has $[\alpha]_D -61.72^\circ$ in benzene solution. Now this behaviour is opposed to the deduction from work of Tschugaeff, Haller, Walden, and others, and, indeed, also from Rupe's own work on this subject, namely, that unsaturated groups (phenyl group, double linking) tend to enhance optical rotation. For example, Rupe finds that *l*-menthyl crotonate has $[\alpha]_D -91.06^\circ$ in benzene solution, whereas *l*-menthyl *n*-butyrate has $[\alpha]_D -70.56^\circ$, the elimination of the double linking lowering the rotatory power in this case. Again, Frankland and Slator (*Trans.*, 1903, 83, 1349) show that *d*-tartranilide has a higher dextrorotation than has *d*-tartramide, and that aromatic groups raise the rotation of the latter compound very considerably. Finally another example of the same effect, and a very striking one, is the comparison between *p*-hydroxyphenyliminocamphor,



with $[\alpha]_D + 1363^\circ$ in chloroform solution, and the product of its reduction, *p*-hydroxyphenylaminocamphor, $C_8H_{14} \begin{smallmatrix} \text{CH} \cdot \text{NH} \cdot C_6H_4 \cdot \text{OH} \\ \text{CO} \end{smallmatrix}$,

with $[\alpha]_D + 83^\circ$ in chloroform solution (Forster and Thornley, *Trans.*, 1909, **95**, 942).

In the course of his important work in this field, Rupe emphasises the depression in rotation exerted by the displacement of a methyl by a phenyl group, thus:

<i>l</i> -Menthyl esters of the acids.	$[\alpha]_D$ in benzene solution.
$CH_3 \cdot CMe \cdot CO_2H$	- 91.76°
$CH_3 \cdot CPh \cdot CO_2H$..	63.03
$CMe_2 \cdot CH \cdot CO_2H$	88.60
$CMePh \cdot CH \cdot CO_2H$	65.89
$CPh_2 \cdot CH \cdot CO_2H$	37.92

These figures are quoted here for comparison with the values obtained for the glycols:

<i>l</i> -Glycols.	$[\alpha]_D$ in acetone solution.
$OH \cdot CHPh \cdot CMe_2 \cdot OH$	- 21.6°
$OH \cdot CHPh \cdot CMePh \cdot OH$	+ 34.0
$OH \cdot CHPh \cdot CEtPh \cdot OH$	+ 27.4
$OMe \cdot CHPh \cdot CPh_2 \cdot OH$	+ 185.3
$OH \cdot CHPh \cdot CPh_2 \cdot OH$	+ 221.3

The latter compounds are, of course, of a very different type from those of Rupe, and it is of interest that the effect of the phenyl group is so pronounced.

EXPERIMENTAL.

Action of Magnesium Methyl Iodide on l-Benzoin.

The Grignard reagent, prepared from 1.4 grams of magnesium (4 mols.), 7.8 grams of methyl iodide (4 mols.), and 50 c.c. of ether, was cooled in ice-cold water, and 3 grams of finely-powdered *l*-benzoin (1 mol.) were added in small quantities at a time. The action was vigorous. After the mixture had been boiled gently for three hours, it was decomposed in the usual manner by ice and dilute sulphuric acid, and the liberated glycol extracted with ether. After drying the ethereal solution and removing the ether, the resulting viscid, brown product solidified when stirred with a small quantity of carbon disulphide. It was purified by crystallising from carbon disulphide several times, 10 c.c. of solvent being used on each occasion, until its rotation was constant.

1-α-Dihydroxy-αβ-diphenylpropane, $OH \cdot CHPh \cdot CMePh \cdot OH$, separates from carbon disulphide as a colourless, amorphous solid, and melts at 81–82°. It is very readily soluble in boiling carbon disulphide, and sparingly so in the cold solvent. It is very readily soluble in cold benzene, methyl alcohol, ethyl alcohol, ether, or

acetone, and less so in cold carbon tetrachloride. It dissolves readily in boiling light petroleum (b. p. 60—80°), separating on cooling. It is very sparingly soluble in water. It gives a violet coloration with cold concentrated sulphuric acid.

For analysis, the glycol was dried at 78° until constant in weight:

0.1175 gave 0.3383 CO₂ and 0.0743 H₂O. C=78.5; H=7.1.

C₁₅H₁₆O₂ requires C=78.9; H=7.1 per cent.

The specific rotation was determined in acetone solution, the glycol having been dried at 78°:

$$l=2, c=1.648, \alpha_D^{12.5} + 1.12^\circ, [\alpha]_D^{12.5} + 34.0^\circ.$$

No racemisation was observed with the solution of the glycol in alcoholic potash.

Action of Magnesium Methyl Iodide on r-Benzoin.

Since a second asymmetric carbon atom is generated by the action of magnesium methyl iodide on benzoin, the behaviour of *r*-benzoin was studied in order to find out if only one glycol is formed. The experiment indicated that, if an isomeric glycol is produced, it can be present only in small amount.

Twelve grams of *r*-benzoin were gradually added to the Grignard reagent, prepared from 5.5 grams of magnesium, 30.3 grams of methyl iodide, and 100 c.c. of ether. The crude product, obtained as in the previous experiment, amounted to 12.5 grams. After one crystallisation from carbon disulphide, the glycol melted at 103.5—105.5°, and the yield was 11.5 grams. After a second crystallisation from the same solvent, the compound was pure.

Inactive $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane separates from carbon disulphide in colourless needles, and melts at 103.5—104.5°. It is less soluble in carbon disulphide or light petroleum than is its *l*-isomeride. When dried in a vacuum over sulphuric acid at the ordinary temperature, it retains persistently small quantities of solvent. For analysis, it was accordingly dried at 78° until constant in weight:

0.1223 gave 0.3520 CO₂ and 0.0764 H₂O. C=78.5; H=7.0.

C₁₅H₁₆O₂ requires C=78.9; H=7.1 per cent.

The preparation of this glycol has also been described by Tiffeneau and Dorlencourt (*Ann. Chim. Phys.*, 1909, [viii], 16, 237), who give the melting point as 104°. There is also no evidence in the work recorded by these authors of the formation of a second isomeride.

Action of Magnesium Ethyl Iodide on l-Benzoin.

Four grams of *l*-benzoin (1 mol.) were treated with magnesium ethyl iodide, obtained from 1.8 grams of magnesium (4 mols.), 11.8 grams of

ethyl iodide (4 mols.), and 50 c.c. of ether. The crude diphenylethyl glycol (4.3 grams) was crystallised from successive small quantities of carbon disulphide. The first crop obtained melted sharply, and, when dried at 78° until constant in weight, gave the following value for its specific rotation in acetone solution :

$$l = 2, c = 1.288, \alpha_D + 0.64^\circ, [\alpha]_D + 24.8^\circ.$$

After a second crystallisation, the melting point was the same as before, but the value for the specific rotation determined as before was somewhat higher. The concentration, however, was greater :

$$l = 2, c = 4.674, \alpha_D^{11.7} + 2.56^\circ, [\alpha]_D^{11.7} + 27.4^\circ.$$

The value obtained after another crystallisation was practically identical with this.

1- α -Dihydroxy- α - β -diphenylbutane, $\text{OH} \cdot \text{CHPh} \cdot \text{CEtPh} \cdot \text{OH}$, separates from carbon disulphide in colourless prisms, capped by pyramids, and melts at 96.5—97.5°. It is very readily soluble in boiling carbon disulphide, and sparingly soluble in the cold solvent. It is soluble with difficulty in light petroleum or water. It is easily soluble in cold acetone, ethyl alcohol, benzene, chloroform, or ether, and less so in carbon tetrachloride. Its solution in cold concentrated sulphuric acid is magenta-coloured, and becomes green on heating.

For analysis, it was dried at 78° :

0.1509 gave 0.4366 CO_2 and 0.1018 H_2O . $\text{C} = 78.9$; $\text{H} = 7.5$.

$\text{C}_{16}\text{H}_{18}\text{O}_2$ requires $\text{C} = 79.3$; $\text{H} = 7.5$ per cent.

The value for the specific rotation in acetone solution is $+27.4^\circ$, as given above. In ethyl-alcoholic solution :

$$l = 2, c = 2.883, \alpha_D^{12.5} + 1.13^\circ, [\alpha]_D^{12.5} + 19.6^\circ.$$

In chloroform solution :

$$l = 4, c = 2.044, \alpha_D^{10.5} + 0.26^\circ, [\alpha]_D^{10.5} + 3.2^\circ.$$

The corresponding inactive compound has been prepared by Acree (*Amer. Chem. J.*, 1905, **33**, 193). It melts at 115—116°.

When the *l*-glycol was dissolved in ethyl-alcoholic potassium hydroxide, no racemisation was detected. Thus 0.2977 gram, when made up to 10 c.c. in cold alcoholic potash (0.104*N*), had $\alpha_D + 1.20^\circ$ in a 2-dm. tube. This value did not alter during twenty-five hours at the temperature of the laboratory.

Action of Magnesium Phenyl Bromide on Methyl l-Mandelate and on l-Benzoïn.

A solution of methyl *l*-mandelate (8 grams) in ether (50 c.c.) was siphoned within an interval of eight minutes into a solution of the Grignard reagent, prepared from magnesium (4.6 grams), bromobenzene

(30.3 grams) and ether (50 c.c.). After the vigorous action had subsided, the mixture was boiled gently for two hours and then decomposed in the usual manner. The resulting brown solid was crystallised several times from methyl alcohol until its rotation was constant.

For analysis and determinations of its specific rotation, the glycol was dried at 100° until constant in weight. It retains methyl alcohol with considerable obstinacy, determinations indicating, however, that the alcohol is not present in the air-dried product in definite molecular proportions.

1- $\alpha\beta$ -Dihydroxy- $\alpha\beta\beta$ -triphenylethane (triphenylethylene glycol),
 $\text{OH}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$,

separates from methyl alcohol in colourless needles, and, after being dried at 100° , melts at $128\text{--}129^{\circ}$, the melting point of the inactive isomeride being 167° according to Acree (*Ber.*, 1904, **37**, 2762). The active glycol is readily soluble in boiling methyl alcohol. It may also be crystallised from light petroleum, in which it is sparingly soluble. It is practically insoluble in water, but dissolves with ease in cold acetone, benzene, ether, or chloroform. It gives an emerald-green coloration when heated with concentrated sulphuric acid; the solution becomes colourless in presence of excess of water, and a yellow tint appears when an excess of alkali is added. These colour reactions are also exhibited by triphenylvinyl alcohol:

0.1719 gave 0.5230 CO_2 and 0.0960 H_2O . $\text{C} = 83.0$; $\text{H} = 6.2$.

$\text{C}_{20}\text{H}_{18}\text{O}_2$ requires $\text{C} = 82.7$; $\text{H} = 6.3$ per cent.

A determination of its specific rotation in acetone solution gave the result:

$$l = 4, c = 1.0156, \alpha_D^{12.5} + 8.99^{\circ}, [\alpha]_D^{12.5} + 221.3^{\circ}.$$

Its rotation was also determined in chloroform solution:

$$l = 4, c = 1.3196, \alpha_D^{15} + 12.33^{\circ}, [\alpha]_D^{15} + 233.6^{\circ}.$$

It was of interest to find out if a dextrorotatory glycol would also be obtained by the interaction of *l*-benzoin and magnesium phenyl bromide. Finely-powdered *l*-benzoin (3 grams) was accordingly added gradually to the solution obtained from magnesium (1 gram), bromobenzene (8.1 grams), and ether (60 c.c.), the Grignard reagent having been cooled previously in ice-cold water. After the addition of the benzoin, the mixture was boiled gently for ninety minutes. The glycol was isolated as in the preceding experiment. On analysis:

0.1343 gave 0.4085 CO_2 and 0.0758 H_2O . $\text{C} = 82.95$; $\text{H} = 6.3$.

$\text{C}_{20}\text{H}_{18}\text{O}_2$ requires $\text{C} = 82.7$; $\text{H} = 6.3$ per cent.

The compound was identical with that obtained from methyl *l*-mandelate, as shown by determinations of melting point and specific rotation made with it.

The action of ethyl-alcoholic potassium hydroxide was examined. *l*-Triphenylethylene glycol (0.8 gram) was boiled for thirty minutes with 25 c.c. of 0.112*N*-alkali. A violet coloration appeared at first, and, when the solution was shaken, this became reddish-brown. The mixture was poured into 200 c.c. of water, and the precipitated glycol filtered and dried. Polarimetric examination in acetone solution showed that the glycol had remained unracemised even after this drastic treatment with alkali.

Action of Magnesium Methyl Iodide on Methyl l-Mandelate.

A solution of methyl *l*-mandelate (7 grams) in ether (40 c.c.) was siphoned within an interval of ten minutes into an ice-cold solution of the Grignard reagent, prepared from magnesium (4.4 grams), methyl iodide (26.1 grams), and ether (50 c.c.). The crude product obtained in the usual manner was an oil, which was dried and obtained crystalline by being stirred with light petroleum. After two further crystallisations from light petroleum containing a little ether, the glycol was obtained pure.

1-αβ-Dihydroxy-α-phenylisobutane, $\text{OH} \cdot \text{CHPh} \cdot \text{CMe}_2 \cdot \text{OH}$, melts at 33.5—35°. It gives an orange coloration with cold concentrated sulphuric acid, and the solution becomes strongly fluorescent when warmed :

0.2657 gave 0.7000 CO_2 and 0.2029 H_2O . $\text{C} = 71.9$; $\text{H} = 8.5$.

$\text{C}_{10}\text{H}_{14}\text{O}_2$ requires $\text{C} = 72.2$; $\text{H} = 8.5$ per cent.

Its specific rotation was determined in acetone solution :

$$l = 2, c = 2.7352, \alpha_D^{13} - 1.18^\circ, [\alpha]_D^{13} - 21.6^\circ.$$

Action of Thionyl Chloride on l-Benzoin and on Inactive Triphenylethylene Glycol.

The action of thionyl chloride on *l*-benzoin was studied in the hope of obtaining optically active desyl chloride, but racemisation occurred in the displacement of the hydroxy-group by chlorine. *l*-Benzoin (3.2 grams) was covered with thionyl chloride (3.5 grams). The evolution of hydrogen chloride began at the ordinary temperature, whilst the product gradually became liquid. After three hours, the temperature was raised gradually from 15° to 55° during the course of two hours, when very little action appeared to take place. At 55°, hydrogen chloride was again evolved somewhat briskly. The temperature was then raised to 90°. The dark reddish-brown liquid became semi-solid when placed over soda-lime in a vacuum. After some days, the specific rotation of the product in acetone solution was -9.7° , but this activity may have been due to a little unchanged

benzoin. After three crystallisations from ethyl alcohol, desyl chloride, melting at 66—68°, was obtained. This was quite inactive when examined polarimetrically.

Thionyl chloride (28 grams) was added to inactive triphenylethylene glycol (5 grams) prepared from *r*-benzoin according to Acree (*loc. cit.*). The glycol dissolved within fifteen minutes at the ordinary temperature, the red solution slowly evolving hydrogen chloride. The temperature was raised slowly to the boiling point of thionyl chloride during one hour, and maintained at this point for two hours longer. After drying over soda-lime in a vacuum, the resulting solid was crystallised twice from light petroleum (b. p. 60—80°). The compound obtained in this manner was quite free from chlorine, and its melting point (135—136°) and analysis showed that it was triphenylvinyl alcohol:

0.1654 gave 0.5352 CO₂ and 0.0889 H₂O. C = 88.2; H = 6.0.

C₂₀H₁₆O requires C = 88.2; H = 5.9 per cent.

Triphenylvinyl alcohol has been prepared by Delacre (*Bull. Soc. chim.*, 1895, [iii], 13, 857; compare also Saint-Pierre, *Bull. Soc. chim.*, 1891, [iii], 5, 292; Gardeur, *Bull. Acad. roy. Belg.*, 1897, [iii], 34, 67), who employed the Friedel-Crafts' reaction with trichloroacetyl chloride and benzene. The proof, however, that the compound in question was triphenylvinyl alcohol, CPh₂:CPh·OH, and not triphenylethanone, CHPh₂:COPh, was supplied by Biltz (*Ber.*, 1899, 32, 650). Anschütz and Förster (*Annalen*, 1909, 368, 89) have observed recently that triphenylvinyl alcohol is formed by the interaction of acetylmandelyl chloride, benzene, and aluminium chloride, whereas the formation of benzoin acetate might have been expected. The same authors also prepared the vinyl alcohol from desyl chloride, benzene, and aluminium chloride.

The action of fuming hydrochloric acid on inactive triphenylethylene glycol is similar to that of thionyl chloride. Three grams of the glycol were added to 40 c.c. of aqueous hydrochloric acid, saturated at 0°. After several weeks in a stoppered bottle at the ordinary temperature, the product was diluted with water, and the solid crystallised twice from ethyl alcohol. It melted at 135.5—136.5°, and when it was mixed with an equal amount of the glycol, obtained by the aid of thionyl chloride, the melting point did not change.

Inactive β-Hydroxy-α-methoxy-αββ-triphenylethane.

Methylation of Inactive Triphenylethylene Glycol.—Four grams of the inactive glycol (1 mol.) were added to 9.6 grams of silver oxide (3 mols.), 24 grams of methyl iodide (12 mols.), and 35 c.c. of acetone. The mixture was boiled gently for six hours and filtered. The solvent

was removed from the filtrate, and the product again alkylated with half the above quantities of oxide and iodide. The product obtained in this manner was crystallised once from much light petroleum (b. p. 60—80°), and then twice from methyl alcohol :

0.1166 gave 0.3557 CO₂ and 0.0675 H₂O. C = 83.2 ; H = 6.5.

0.3284 „ 0.2392 AgI ; OMe = 9.6.

C₂₁H₂₀O₂ requires C = 82.9 ; H = 6.6 ; OMe = 10.2 per cent.

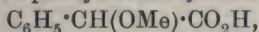
This compound is obviously a monomethyl derivative of triphenylethylene glycol. The following experiments showed that it was β-hydroxy-α-methoxy-αββ-triphenylethane, and not α-hydroxy-β-methoxy-αββ-triphenylethane.

Action of Magnesium Phenyl Bromide on Inactive Benzoin Methyl Ether.—The Grignard reagent, prepared from 0.4 gram of magnesium (1.3 mols.), 2.5 grams of bromobenzene (1.3 mols.), and 14 c.c. of ether, was boiled gently for two hours with 2.7 grams of inactive benzoin methyl ether (1 mol.). The product, obtained in the usual manner, was a crystalline solid, and amounted to 3.2 grams. After two crystallisations from much ethyl alcohol, β-hydroxy-α-methoxy-αββ-triphenylethane, melting at 139°, was obtained. Its identity with the compound prepared from triphenylethylene glycol was shown by the melting point of a mixture of the two, and by the analysis :

0.1818 gave 0.5510 CO₂ and 0.1080 H₂O. C = 82.65 ; H = 6.6.

C₂₁H₂₀O₂ requires C = 82.9 ; H = 6.6 per cent.

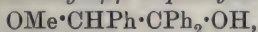
Action of Magnesium Phenyl Bromide on Inactive Methyl Phenyl-methoxyacetate.—Inactive phenylmethoxyacetic acid,



was prepared by the interaction of sodium methoxide and methyl phenylchloroacetate. It was isolated by the aid of its sparingly soluble sodium salt (compare McKenzie, Trans., 1899, **75**, 753), and then esterified by means of methyl alcohol and sulphuric acid. Eighteen grams of methyl ester, boiling at 118—119°/8 mm., were obtained from 20 grams of acid.

Five grams of the methyl ester (1 mol.), dissolved in 40 c.c. of ether, were added to a solution of 2 grams of magnesium (3 mols.) in 13.2 grams of bromobenzene (3 mols.) and 40 c.c. of ether within an interval of six minutes. The crude product obtained by decomposition of the additive compound was crystallised twice from ethyl alcohol. The yield of pure methoxy-glycol amounted to 5.4 grams. It was identical with the products obtained from triphenylethylene glycol and benzoin methyl ether respectively.

Inactive β-hydroxy-α-methoxy-αββ-triphenylethane,



melts at 138.5—139.5°. It is fairly soluble in boiling ethyl alcohol,

and sparingly so in the cold. It crystallises from ethyl alcohol in colourless prisms. It may also be crystallised from light petroleum (b. p. 60—80°), in which it is fairly soluble on heating. It is fairly soluble in cold ether, easily so in cold acetone or chloroform, somewhat less readily so in cold carbon tetrachloride, and sparingly soluble in water. It gives a colour reaction with concentrated sulphuric acid similar to that of *l*-triphenylethylene glycol.

1-β-Hydroxy-α-methoxy-αββ-triphenylethane.

Action of Magnesium Phenyl Bromide on Methyl 1-Phenylmethoxyacetate.—Methyl *l*-mandelate was alkylated with silver oxide and methyl iodide, the mixture of methoxy-ester and unchanged methyl mandelate saponified, and the resulting acid converted into sodium salt. Since sodium *l*-phenylmethoxyacetate is sparingly soluble in water (McKenzie, *loc. cit.*), it can be separated readily from the sodium mandelate present.

l-Phenylmethoxyacetic acid, obtained from the sodium salt, had $[\alpha]_D^{17} - 150.1^\circ$ for $c = 3.597$ in ethyl-alcoholic solution, the value quoted previously being $[\alpha]_D^{13.5} - 150.0^\circ$ for $c = 6.7656$.

l-Phenylmethoxyacetic acid (10 grams) was converted into its methyl ester by the Fischer-Speier method, using methyl alcohol and sulphuric acid. The yield was 8.5 grams.

Methyl 1-phenylmethoxyacetate, $C_6H_5 \cdot CH(OMe) \cdot CO_2Me$, is a colourless oil, which boils at 117.5—118°/8 mm. :

0.2885 gave 0.6988 CO_2 and 0.1775 H_2O . $C = 66.1$; $H = 6.9$.

$C_{10}H_{12}O_3$ requires $C = 66.6$; $H = 6.7$ per cent.

The following determinations of specific rotation of this ester in various solvents were made for comparison with the activity of methyl *l*-mandelate In carbon disulphide solution :

$l = 1$, $c = 2.93$, $\alpha_D^{12.5} - 2.98^\circ$, $[\alpha]_D^{12.5} - 101.7^\circ$.

In acetone solution :

$l = 4$, $c = 2.6948$, $\alpha_D^{13} - 10.38^\circ$, $[\alpha]_D^{13} - 96.3^\circ$.

In benzene solution :

$l = 4$, $c = 2.0968$, $\alpha_D^9 - 8.32^\circ$, $[\alpha]_D^9 - 99.2^\circ$.

A solution of methyl *l*-methoxymandelate (5 grams, 1 mol.) in ether (40 c.c.) was siphoned with constant shaking within an interval of six minutes into a solution of the Grignard reagent (3 mols.) prepared from magnesium (2 grams), bromobenzene (13.2 grams), and ether (40 c.c.). Towards the end of the addition a bulky precipitate separated, which became grey on warming. The mixture was heated for two hours. The crude product resulting from the action amounted

to 9 grams. After two crystallisations from ethyl alcohol, the compound is pure.

l- β -Hydroxy- α -methoxy- $\alpha\beta\beta$ -triphenylethane, $\text{OMe}\cdot\text{CHPh}\cdot\text{CPh}_2\cdot\text{OH}$, separates from ethyl alcohol in colourless needles, grouped in rosettes, and melts at $143\text{--}144^\circ$. Its colour reaction with concentrated sulphuric acid is similar to that of the inactive isomeride:

0.1459 gave 0.4423 CO_2 and 0.0852 H_2O . $\text{C} = 82.7$; $\text{H} = 6.5$.

0.2397 „ 0.1742 AgI . $\text{OMe} = 9.6$.

$\text{C}_{21}\text{H}_{20}\text{O}_2$ requires $\text{C} = 82.9$; $\text{H} = 6.6$; $\text{OMe} = 10.2$ per cent.

Its specific rotation was determined in a number of solvents. In acetone solution:

$$l = 1, c = 5.428, \alpha_D^{12} + 10.06^\circ, [\alpha]_D^{12} + 185.3^\circ.$$

In chloroform solution:

$$l = 1, c = 4.579, \alpha_D^{13} + 10.76^\circ, [\alpha]_D^{13} + 235.0^\circ.$$

In benzene solution:

$$l = 1, c = 3.667, \alpha_D^9 + 10.8^\circ, [\alpha]_D^9 + 294.5^\circ.$$

In ethyl-alcoholic solution:

$$l = 4, c = 1.0176, \alpha_D^8 + 6.77^\circ, [\alpha]_D^8 + 166.3^\circ.$$

The glycol is sparingly soluble in cold ethyl alcohol. It may also be crystallised from methyl alcohol or light petroleum (b. p. $60\text{--}80^\circ$). It is easily soluble in cold acetone, chloroform, carbon tetrachloride, ether, or benzene, and sparingly so in water.

Methylation of l-Triphenylethylene Glycol.—Seven grams of *l*-triphenylethylene glycol (1 mol.) were heated with 11.2 grams of silver oxide (2 mols.), 42 grams of methyl iodide (12 mols.), and 10 c.c. of acetone during seven hours. The alkylation was found, however, to be incomplete even after a second alkylation under the same conditions as before. After a third alkylation, the product was crystallised until its rotation was constant, four crystallisations from light petroleum being necessary. The glycol obtained in this manner was identical with *l*- β -hydroxy- α -methoxy- $\alpha\beta\beta$ -triphenylethane described above. It melted at $143\text{--}144^\circ$, and its identity was confirmed by the mixed melting-point method. A determination of its specific rotation in acetone solution gave the result:

$$l = 2, c = 2.885, \alpha_D^{13} + 10.68^\circ, [\alpha]_D^{13} + 185.1^\circ.$$

No racemisation was detected with the solution of this glycol in alcoholic potash. 0.254 Gram was made up to 25 c.c. with 0.168*N*-alkali. This solution gave $\alpha_D + 6.84^\circ$, a value which had not changed after twenty hours at the ordinary temperature.

The bulk of the expense of this investigation has been defrayed by grants from the Government Grant Committee of the Royal Society and from the Research Fund Committee of the Chemical Society, for which we desire to make this grateful acknowledgment.

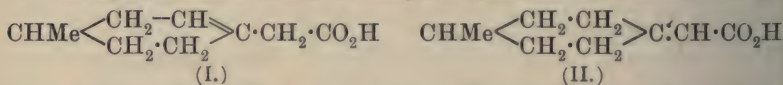
BIRKBECK COLLEGE,
LONDON, E.C.

LIII.—*The Synthesis of Δ^1 -cyclopenteneacetic Acid and 1-Methyl- Δ^2 -cyclohexene-3-acetic Acid.*

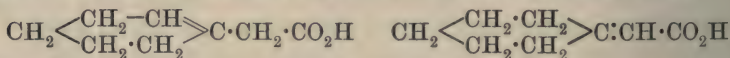
By VICTOR JOHN HARDING and WALTER NORMAN HAWORTH.

A SHORT time ago, Harding, Haworth, and Perkin (Trans., 1908, 93, 1943) published an account of a series of experiments on the constitution and synthesis of 1-methylcyclohexylidene-4-acetic acid. In the course of this investigation a convenient method for the preparation of unsaturated cyclic acids was discovered, and the present authors have continued the work in this direction.

In the previous communication (*loc. cit.*) it was shown that the condensation of ethyl sodiocyanoacetate with cyclohexanone and 1-methylcyclohexan-4-one gave products which, on hydrolysis, yielded derivatives of acetic acid containing the double bond in the ring. In the case of 1-methylcyclohexan-4-one, 1-methyl- Δ^3 -cyclohexene-4-acetic acid (I)



is produced. The isomeric 1-methylcyclohexylidene-4-acetic acid (II), an acid first prepared by Perkin and Pope (Trans., 1908, 93, 1075; compare also Wallach, *Annalen*, 1909, 365, 266), is not formed in any appreciable quantity. The products of the condensation of cyclohexanone and ethyl sodiocyanoacetate were also investigated, and it was shown that in this case a mixture of the two isomeric acids:



was produced (Harding, Haworth, and Perkin, *loc. cit.*, p. 1961), the latter acid being present, however, only in small amount.

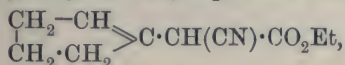
This fact is worthy of note, since there is no evidence of the formation, even in traces, of 1-methylcyclohexylidene-4-acetic acid during the condensation of 1-methylcyclohexan-4-one and ethyl sodiocyanoacetate.

It is clear that in the latter case the cyano-ester obtained from the cyclic ketone and ethyl cyanoacetate, whether piperidine or sodium ethoxide is used as the condensing agent, consists almost entirely of

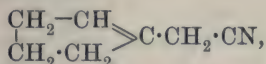
the derivative with the double linking in the ring. This was further proved by the observation that, when treated with methyl iodide or bromoacetophenone, substitution derivatives were readily formed (*loc. cit.*, p. 1958) in almost quantitative yield. In the present communication the authors have extended their investigation to *cyclopentanone* and inactive 1-methyl*cyclohexan-3-one*.

The condensation products of *cyclopentanone* are particularly interesting, because in this case the resulting ester is solid, whereas in the case of six-membered rings it is a liquid. This fact has enabled the authors to remove all doubt as to the nature of the reaction, since they have found that, prepared either by means of ethyl sodiocyanoacetate or the free ester and piperidine, the cyano-ester obtained is the same.

cyclopentanone condenses readily with ethyl sodiocyanoacetate with the formation of ethyl α -cyano- Δ^1 -*cyclopentene-1-acetate*,

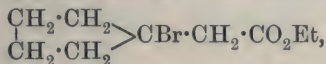


and α -cyano- Δ^1 -*cyclopentene-1-acetic acid*. The methyl ester is obtained in a similar manner from methyl sodiocyanoacetate and *cyclopentanone*, and is also crystalline. Both these cyano-esters may be methylated by treatment with sodium methoxide and methyl iodide. α -Cyano- Δ^1 -*cyclopentene-1-acetic acid* decomposes on distillation under diminished pressure with elimination of carbon dioxide and formation of Δ^1 -*cyclopenteneacetonitrile*,

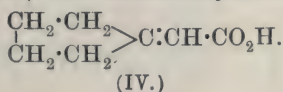
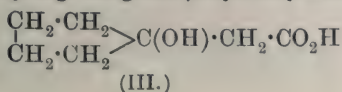


from which, by digestion with alcohol and sulphuric acid and subsequent hydrolysis, Δ^1 -*cyclopenteneacetic acid* is obtained.

This acid had previously been prepared by Wallach (*Annalen*, 1902, 323, 159, and 1906, 347, 324), who obtained it by the condensation of *cyclopentanone* and ethyl bromoacetate in presence of zinc, and subsequent elimination of water from the hydroxy-ester by means of potassium hydrogen sulphate. When the hydroxy-ester is treated with hydrobromic acid it yields ethyl 1-bromocyclopentane-1-acetate,

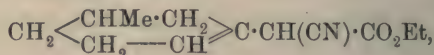
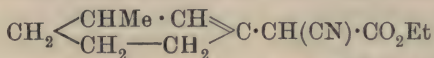


and this is decomposed by dimethylaniline with the formation of ethyl Δ^1 -*cyclopenteneacetate*. In order to remove all doubt as to the constitution of this acid, the authors have, with the kind permission of Prof. O. Wallach, prepared the isomeric *cyclopentylideneacetic acid* (IV) by digesting the β -hydroxy-acid (III) with acetic anhydride :

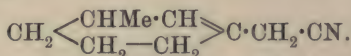


The latter acid yields *cyclopentanone* on oxidation with alkaline permanganate, and its formation by the above method is exactly similar to that of 1-methyl*cyclohexylidene*-4-acetic acid from 1-methyl-4-hydroxy*cyclohexane*-4-acetic acid.

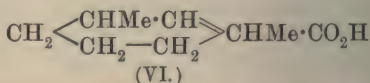
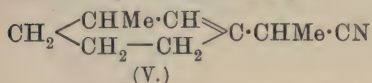
The condensation of 1 methyl*cyclohexan*-3-one with ethyl sodio-cyanoacetate proceeds quite readily, with the formation of an ester which may have either of the following constitutions:



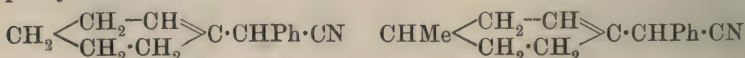
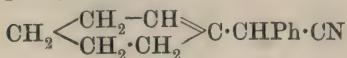
and it has not yet been found possible to decide between these, but in this paper we assume that it has the former. The cyano-acid obtained from the hydrolysis of this ester loses carbon dioxide when distilled under diminished pressure, with the production of 1-methyl- Δ^2 -*cyclohexene*-3-acetonitrile.



When this nitrile is hydrolysed it yields the corresponding acid, which was found to melt at 25° . Wallach (*Annalen*, 1901, **314**, 157; 1906, **347**, 340), by the condensation of 1-methyl*cyclohexan*-3-one with ethyl bromoacetate in presence of zinc, and the subsequent elimination of water from the hydroxy-ester, obtained a liquid acid, the amide of which he first found to melt at 150° , but in a later paper he gives 153 — 154° as the true melting point. The amide of the acid which we have prepared was found to melt at 150° , but we do not think there can be any doubt as to the identity of the two acids. The possibility that this acid contains the ethylenic linking outside the ring, and is, therefore, 1-methyl*cyclohexylidene*-3-acetic acid, may be dismissed, since the cyano-ester, from which it is produced readily, gives on treatment with sodium methoxide and methyl iodide a methyl-substituted derivative which passes on hydrolysis and distillation into the corresponding nitrile (V).



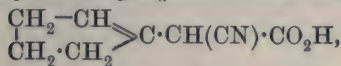
This nitrile can be further hydrolysed only with difficulty to the corresponding α -1-methyl- Δ^2 -*cyclohexene*-3-propionic acid (VI), which is a liquid. The authors have also attempted to prepare alicyclic phenyl-acetic acids by condensing *cyclohexanone* and 1-methyl*cyclohexan*-4-one with phenylacetonitrile in the presence of sodium ethoxide. The phenylacetonitriles:



are easily obtained in this way, but, so far, no method by which they can be hydrolysed to the corresponding acids has been found. All attempts to hydrolyse these nitriles resulted in the production of the original ketone and phenylacetic acid.

EXPERIMENTAL.

α -Cyano- Δ^1 -cyclopenteneacetic Acid,



and its Ethyl Ester.

In preparing ethyl α -cyano- Δ^1 -cyclopenteneacetate, ethyl cyanoacetate (56 grams) was added to a solution of sodium (11.5 grams) in alcohol, and, after the separation of the white sodium derivative, cyclopentanone (42 grams) was then introduced. The sodium derivative rapidly dissolved, leaving a clear solution, which was heated for an hour on the water-bath, and the yellow solid which had separated was dissolved in water and decomposed by dilute hydrochloric acid. The precipitated oil was extracted with ether, the ethereal solution washed with water, and then shaken with sodium carbonate, dried, and evaporated. The residual oil on fractionation yielded a small quantity of cyclopentanone, and then ethyl α -cyano- Δ^1 -cyclopenteneacetate distilled over at 163—165°/15 mm. as a viscid, colourless oil which, when pure, solidified in colourless needles, melting at 54°:

0.1230 gave 0.3021 CO_2 and 0.0811 H_2O . C = 67.0; H = 7.3.

0.1373 „ 9.1 c.c. N_2 at 16° and 761 mm. N = 7.7.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires C = 67.0; H = 7.3; N = 7.8 per cent.

The sodium carbonate extract on acidifying yielded an oil which was extracted with ether, and, after evaporation of the solution, the residue rapidly solidified. The solid acid was pressed on porous porcelain, and then recrystallised from benzene, or, better, from anhydrous ether, from which it separates in large, colourless prisms, melting at 129°:

0.1301 gave 0.3029 CO_2 and 0.0682 H_2O . C = 63.4; H = 5.8.

0.1020 „ 8.0 c.c. N_2 at 18° and 760 mm. N = 9.1.

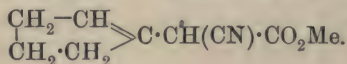
$\text{C}_8\text{H}_9\text{O}_2\text{N}$ requires C = 63.5; H = 5.9; N = 9.3 per cent.

α -Cyano- Δ^1 -cyclopenteneacetic acid is soluble in ether, benzene, ethyl acetate, or ethyl alcohol, but only sparingly so in light petroleum. It dissolves in dilute potassium hydroxide, and the solution soon clouds on warming, owing to the separation of cyclopentanone by decomposition of the acid. The potassium salt is sparingly soluble in concentrated alkali.

The following is an alternative method of preparation with the aid of piperidine:

Equimolecular quantities of *cyclopentanone* and ethyl cyanoacetate were mixed with a few drops of piperidine, and the whole kept cold for four hours; the condensation was completed by warming on the water-bath for an hour. The product was cooled and poured into water, when ethyl α -cyano- Δ^1 -*cyclopenteneacetate* separated as a brown, crystalline solid, which was collected, freed from oil by porous porcelain, and recrystallised from dilute ethyl alcohol, from which it separates in tufts of fine, silky needles, melting at 53–54°, the yield by this method being almost quantitative.

Preparation of Methyl α -Cyano- Δ^1 -cyclopenteneacetate,



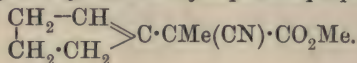
(a) *With Sodium Methoxide.*—*cyclopentanone* (8 grams) was added to methyl sodiocyanoacetate (12 grams), prepared in methyl-alcoholic solution, and the mixture was shaken and gently warmed for ten minutes. Water and dilute mineral acid were then added, and the oil was extracted with ether, washed with sodium carbonate, dried, and distilled, when methyl α -cyano- Δ^1 -*cyclopenteneacetate* passed over as a colourless oil, boiling at 152°/17 mm. The ester gradually crystallised, on keeping overnight, in colourless crystals, melting at 35°; it is soluble in most organic solvents, and is easily recrystallised from dilute methyl alcohol.

(b) *With Piperidine.*—Equimolecular proportions of *cyclopentanone* and methyl cyanoacetate were mixed with a few drops of piperidine, and the condensation was complete at the end of four hours. The product was poured into water, extracted with ether, and treated exactly as described under (a). The product was identical in every respect with that prepared by method (a):

0.1682 gave 11.8 c.c. N_2 (moist) at 14° and 740 mm. $\text{N} = 8.3$.

$\text{C}_9\text{H}_{11}\text{O}_2\text{N}$ requires $\text{N} = 8.5$ per cent.

Methyl α -Cyano- α - Δ^1 -cyclopentenepropionate,



This ester is prepared by the action of methyl iodide and sodium methoxide on ethyl α -cyano- Δ^1 -*cyclopenteneacetate*. Sodium (2 grams) was dissolved in methyl alcohol, and to the cooled solution the cyano-ester (15 grams) was added. The mixture at once assumed a deep red colour, and methyl iodide (30 grams) was then added in small quantities at intervals, care being taken to avoid any increase of temperature. After keeping for an hour, and then warming for a short time on the water-bath, the deep colour faded to yellow, and the liquid was poured

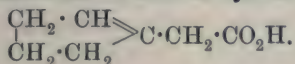
into water, acidified, and extracted with ether, washed with sodium carbonate, dried, and evaporated. The methyl-substitution product distils constantly at $160^\circ/20$ mm. as a colourless oil, with an odour resembling its lower homologue; it showed no signs of crystallising even when placed in ice :

0.1279 gave 0.3156 CO_2 and 0.0889 H_2O . $\text{C} = 67.3$; $\text{H} = 7.7$.

$\text{C}_{10}\text{H}_{18}\text{O}_2\text{N}$ requires $\text{C} = 67.0$; $\text{H} = 7.3$ per cent.

Hydrolysis.—The hydrolysis was effected by means of methyl-alcoholic potash, and the resulting cyano-acid was submitted to distillation under diminished pressure, when carbon dioxide was eliminated, and a nitrile, possessing an odour quite distinct from that of the lower homologue (see below), passed over at $123^\circ/50$ mm. The analysis gave numbers which were approximately correct for α - Δ^1 -cyclopentenepropionitrile.

Δ^1 -cycloPenteneacetonitrile and Δ^1 -cycloPenteneacetic Acid,



When α -cyano- Δ^1 -cyclopenteneacetic acid is distilled under 100 mm. pressure, it suffers decomposition with elimination of carbon dioxide and formation of Δ^1 -cyclopenteneacetonitrile. On refractionating the distillate, it was readily obtained pure as a colourless oil, possessing a pungent odour characteristic of a nitrile, and distilling at $124^\circ/100$ mm. or $150^\circ/200$ mm. :

0.1080 gave 12.4 c.c. N_2 at 20° and 758 mm. $\text{N} = 13.1$.

$\text{C}_7\text{H}_9\text{N}$ requires $\text{N} = 13.1$ per cent.

The hydrolysis of this nitrile was effected by digesting it for twenty-four hours with 20 per cent. alcoholic sulphuric acid, and, on cooling, ammonium sulphate separated in crystals. After dilution with water, the product was extracted with ether, the ethereal solution washed with water until free from alcohol, and then with dilute sodium carbonate; the residue obtained after evaporation of the ether consists of a mixture of ethyl Δ^1 -cyclopenteneacetate with some unchanged nitrile, and this was distilled under diminished pressure. The mixture was now digested with methyl-alcoholic potash for half an hour, and, after the addition of water, the nitrile was removed by extraction with ether. The alkaline solution was evaporated, and, when cool, acidified with dilute hydrochloric acid. An oily acid was precipitated, which soon solidified, and, after remaining in contact with porous porcelain, it was purified by distillation under diminished pressure and analysed immediately :

0.1220 gave 0.2968 CO_2 and 0.0859 H_2O . $\text{C} = 66.4$; $\text{H} = 7.8$.

$\text{C}_7\text{H}_{10}\text{O}_2$ requires $\text{C} = 66.7$; $\text{H} = 7.9$ per cent.

An analysis of the *silver* salt gave the following result:

0.1440 gave 0.0660 Ag. Ag = 45.9.

$C_7H_9O_2Ag$ requires Ag = 46.3 per cent.

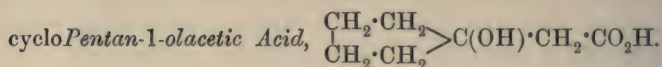
Δ^1 -cyclopenteneacetic acid crystallises in colourless prisms, melting, as found by Wallach, at 51—52°, and distils as a viscid oil at 132°/16 mm. (Wallach: 122°/11 mm.). It is readily soluble in most organic solvents. After exposure to the air, it gives numbers on analysis which are always low in carbon; this is due to oxidation at the double linking, which takes place with greater ease than in the case of the six-carbon-ring homologue (Trans., 1908, 93, 1960), and from the point of view of comparative stability this observation is of considerable interest.

1:2-Dibromocyclopentene-1-acetic acid melts at 87—88° (compare Wallach and Speransky, *Annalen*, 1902, 323, 159).

1-Bromocyclopentaneacetic acid was obtained by stirring the solid unsaturated acid with aqueous hydrobromic acid saturated at 0°. The product was poured on porous porcelain, and afterwards recrystallised from light petroleum, from which solvent it separates in thin, colourless plates, melting at 76°:

0.1770 gave 0.1625 AgBr. Br = 39.0.

$C_7H_{11}O_2Br$ requires Br = 38.7 per cent.



Ethyl cyclopentan-1-olacetate, prepared as described by Wallach and Speransky (*Annalen*, 1902, 323, 159), was obtained as a viscid, colourless oil, distilling at 128—130°/20 mm. (Wallach and Speransky give 105—107°/11 mm.). This ester was hydrolysed with methyl-alcoholic potash, and the hydroxy-acid extracted from the acidified solution by means of ether. On evaporation of the dried ethereal solution, the acid solidified, and was obtained pure by recrystallisation from a mixture of benzene and light petroleum, when it separated in colourless plates containing $\frac{1}{2}H_2O$, and melted at 76°. This acid is very soluble in benzene, ethyl acetate, chloroform, or alcohol, but sparingly so in light petroleum or water:

0.1176 gave 0.2370 CO_2 and 0.0920 H_2O . C = 54.9; H = 8.7.

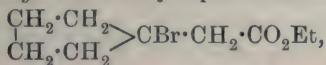
$C_7H_{12}O_3, \frac{1}{2}H_2O$ requires C = 54.9; H = 8.5 per cent.

The *silver* salt was obtained in flat needles:

0.1960 gave 0.0840 Ag. Ag = 42.8.

$C_7H_{11}O_3Ag$ requires Ag = 43.0 per cent.

Ethyl 1-Bromocyclopentaneacetate,



and *Ethyl Δ^1 -cyclopenteneacetate.*

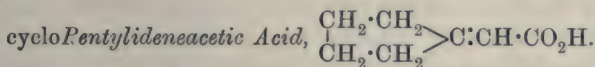
When ethyl *cyclopentan-1-olacetate* is gently warmed in contact with a saturated solution of hydrobromic acid, the bromo-ester is formed, and if the product is left not longer than twenty minutes in contact with the aqueous solution, it escapes hydrolysis to the corresponding acid. The heavy oil which is formed on the addition of water is extracted with ether, washed with water and sodium carbonate, and then dried and distilled, when *ethyl 1-bromocyclopentaneacetate* is obtained as a pleasant smelling, colourless oil, which distils at 142—143°/35 mm.

Hydrobromic acid is readily eliminated from the above bromo-ester, and in the present case the process was carried out by digesting for two hours with twice its volume of dimethylaniline. On adding water and acidifying with dilute hydrochloric acid, the base was recovered at the end of the operation, and the resulting unsaturated ester extracted with ether and purified by distillation, when it was obtained as a colourless oil distilling at 101°/16 mm. This was analysed immediately, with the following result :

0.1375 gave 0.3550 CO_2 and 0.1111 H_2O . $\text{C} = 70.4$; $\text{H} = 9.0$.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires $\text{C} = 70.1$; $\text{H} = 9.1$ per cent.

This ester on hydrolysis gave the corresponding Δ^1 -*cyclopenteneacetic acid*, m. p. 51—52°, which has already been described on p. 492.

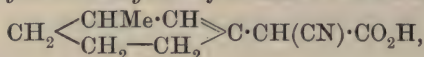


In order to prepare this acid, *cyclopentan-1-olacetic acid* (6 grams) (see p. 492) was digested for two hours with acetic anhydride (8 grams), and at the end of this time the product was distilled in a current of steam and a large volume of distillate collected (Wallach, *Annalen*, 1909, 365, 255). The distillate was saturated with ammonium sulphate and extracted with ether, the ethereal solution washed many times with water to remove acetic acid, and then dried and evaporated. The residue soon crystallised in long, slender needles, which melted at 61°. The acid decolorises cold permanganate solution instantly, with the formation of *cyclopentanone*. The *silver* salt prepared in the usual way was analysed :

0.2170 gave 0.1007 Ag. $\text{Ag} = 46.4$.

$\text{C}_7\text{H}_9\text{O}_2\text{Ag}$ requires $\text{Ag} = 46.3$ per cent.

α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetic Acid,



and its Ethyl Ester.

When 1-methylcyclohexan-3-one is mixed in alcoholic solution with the sodium derivative of ethyl cyanoacetate in equimolecular quantities, condensation takes place in a similar manner to that described in the case of cyclopentanone on p. 489 if the same conditions are observed. The product was diluted, acidified, extracted with ether, and washed with water and dilute sodium carbonate (A). The residue from the ethereal solution yielded a little unchanged 1-methylcyclohexan-3-one on distillation under diminished pressure, also a small quantity of 1-methyl- Δ^2 -cyclohexene-3-acetonitrile (see p. 495), and then ethyl α -cyano-1-methyl- Δ^2 -cyclohexene-3-acetate distilled over at 168—169°/18 mm. as a colourless oil, possessing a faint but characteristic odour:

0.1459 gave 0.3720 CO_2 and 0.1074 H_2O . C = 69.5; H = 8.2.

0.1588 „ 9.6 c.c. N_2 at 9° and 744 mm. N = 7.1.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires C = 69.6; H = 8.2; N = 6.7 per cent.

This ester can also be obtained in a better yield by employing equimolecular quantities of 1-methylcyclohexan-3-one and ethyl cyanoacetate and adding a few drops of piperidine. Under the influence of this reagent, the condensation is complete in about two hours, and the mixture soon becomes turbid, owing to the separation of water. Towards the end of the operation the mixture was heated in a rapidly boiling-water bath. The resulting yellow oil was diluted with water, extracted with ether, washed well with dilute hydrochloric acid, dried, and distilled. The yield is about 60 per cent.

The cyano-acid is obtained in excellent yield from the sodium carbonate washings (A) in the first condensation. The alkaline solution was acidified with dilute hydrochloric acid and extracted with ether, and the ethereal solution dried and evaporated. The residue consisted of a viscid, yellow oil, which was cooled in a freezing mixture, when it soon solidified. The solid was freed from adhering oil by placing it in contact with porous porcelain, and afterwards recrystallised from benzene, from which it separates in short needles, melting sharply at 112°:

0.1122 gave 0.2738 CO_2 and 0.0722 H_2O . C = 66.9; H = 7.1.

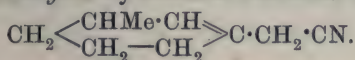
0.1558 „ 10.9 c.c. N_2 at 21° and 760 mm. N = 7.9.

$\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ requires C = 67.0; H = 7.2; N = 7.8 per cent.

α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetic acid is insoluble in cold, and slightly soluble in warm, water; it is also insoluble in light

petroleum, but dissolves with considerable readiness in alcohol, benzene, or ethyl acetate. In contact with concentrated alkali in the cold it is decomposed, with formation of 1-methylcyclohexan-3-one. It does not react with hydrobromic acid to form an additive product.

1-Methyl- Δ^2 -cyclohexene-3-acetonitrile,



This nitrile is prepared by the slow distillation of α -cyano-1-methyl- Δ^2 -cyclohexeneacetic acid under a pressure of 90 mm. The operation is accompanied by the elimination of carbon dioxide, and the nitrile passes over as a light mobile liquid between 150° and 160°. It was purified by redistillation, when it boiled constantly at 152°/90 mm. (Wallach and Beschke, *Annalen*, 1906, **347**, 341, give 108—112°/10 mm. and 230—234° under atmospheric pressure), and was obtained as a colourless oil, possessing a powerful nitrile-like odour:

0.1473 gave 0.4300 CO_2 and 0.1276 H_2O . C = 79.6; H = 9.6.

0.1141 „ 10.4 c.c. N_2 at 20° and 758 mm. N = 10.4.

$\text{C}_9\text{H}_{13}\text{N}$ requires C = 80.0; H = 9.6; N = 10.3 per cent.

1-Methyl- Δ^2 -cyclohexene-3-acetic Acid,



The hydrolysis of the above-mentioned nitrile was carried out under the following conditions:

The pure nitrile, boiling constantly at 152°/90 mm., and prepared from recrystallised cyano-acid, m. p. 112°, was digested for twelve hours with 10 per cent. alcoholic sulphuric acid. The mixture on cooling was poured into water, the precipitated oil extracted with ether, and the ethereal solution dried and evaporated. The residue consisted of ethyl 1-methyl- Δ^2 -cyclohexene-3-acetate, along with some unchanged nitrile, and this mixture was distilled under 100 mm. pressure and then warmed for fifteen minutes with methyl-alcoholic potash. The product was diluted with water, and the nitrile removed by extraction with ether. The aqueous solution was evaporated gently, and then acidified, when the acid separated as an oil, which was dissolved in ether and afterwards distilled. It boiled at 152—158°/20 mm., but was still further purified by solution in ether, extracting by means of sodium carbonate, and again recovering from the alkaline solution. It now distilled constantly at 149°/14 mm., and when cooled in ice rapidly solidified to a mass of fern-shaped crystals. These were drained on an ice-cold porous tile, and the adhering oil was absorbed, leaving the acid as lustrous crystals, which melted about 25°.

Both in odour and appearance this substance closely resembles 1-methyl- Δ^3 -cyclohexene-4-acetic acid, m. p. 41° , obtained by Marckwald and Meth (see introduction), and Δ^1 -cyclohexeneacetic acid, m. p. 38° :

0.1520 gave 0.3879 CO_2 and 0.1270 H_2O . $\text{C} = 69.6$; $\text{H} = 9.2$.

$\text{C}_9\text{H}_{14}\text{O}_2$ requires $\text{C} = 70.1$; $\text{H} = 9.1$ per cent.

Its basicity was determined by titrating with $N/10$ -sodium hydroxide:

0.2658 neutralised 0.0696 NaOH , whereas the same weight of a monobasic acid, $\text{C}_9\text{H}_{14}\text{O}_2$, requires 0.0690 NaOH .

It is exceedingly probable that the above acid, m. p. 25° , is identical with the oily acid previously obtained by Wallach and Salkind (*Annalen*, 1900, **314**, 151; compare also Tétzy, *Bull. Soc. chim.*, 1902, [iii], **27**, 598, and Wallach and Beschke, *Annalen*, 1906, **347**, 340).

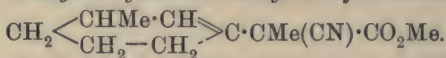
The amide of this acid was prepared by digesting 1-methyl- Δ^2 -cyclohexene-3-acetonitrile with alkali. It crystallises from ether in glistening, silvery plates, melting at 150° . Wallach and Beschke (*Annalen*, 1906, **347**, 340) give the melting point of this amide as 153 — 154° :

0.1395 gave 11.2 c.c. N_2 at 14° and 760 mm. $\text{N} = 9.4$.

$\text{C}_9\text{H}_{15}\text{ON}$ requires $\text{N} = 9.1$ per cent.

Methylation of Ethyl α -Cyano-1-methyl- Δ^2 -cyclohexene-3-acetate.

Formation of Methyl α -Cyano- α -1-methyl- Δ^2 -cyclohexene-2-propionate,



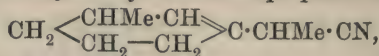
Ethyl - α -cyano-1-methyl- Δ^2 -cyclohexene-3-acetate was mixed in methyl-alcoholic solution with an equimolecular quantity of sodium methoxide, and an excess of methyl iodide was gradually added. The reaction was vigorous, and required cooling at intervals; it was completed by warming gently on the water-bath for fifteen minutes. The product was poured into water, extracted with ether, and distilled, when it passed over constantly at 140 — $142^\circ/10$ mm.:

0.1299 gave 0.3298 CO_2 and 0.0945 H_2O . $\text{C} = 69.3$; $\text{H} = 8.1$.

0.1900 „ 11.9 c.c. N_2 at 18° and 760 mm. $\text{N} = 7.2$.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 69.6$; $\text{H} = 8.2$; $\text{N} = 6.7$ per cent.

α -1-Methyl- Δ^2 -cyclohexene-3-propionitrile,



and α -1-Methyl- Δ^2 -cyclohexene-3-propionic Acid.

The above cyano-ester was hydrolysed by boiling for ten minutes with methyl-alcoholic potash, and, after the addition of water and

evaporating, the alkaline solution was acidified and the oil which separated was extracted with ether. The cyano-acid could not be obtained crystalline, and therefore the crude oil was distilled under 90 mm. pressure, when carbon dioxide was eliminated and an excellent yield of nitrile was obtained. It was purified by redistillation, and was obtained as a colourless, mobile liquid, possessing a pleasant sweet odour, and boiling at 152—153°/90 mm.:

0.1382 gave 10.4 c.c. N_2 at 17° and 757 mm. $N = 9.6$.

$C_{10}H_{15}N$ requires $N = 9.4$ per cent.

Hydrolysis.—The nitrile was boiled for twenty-four hours with twice its volume of alcohol, containing 20 per cent. of sulphuric acid. It was observed that the reaction proceeded very slowly, in striking contrast to the hydrolysis of the lower homologue, 1-methylcyclohexene-3-acetonitrile (p. 495). The product was diluted with water, extracted with ether, and the mixture of nitrile and ester distilled under 100 mm. pressure. The distilled oil was now digested for ten minutes with methyl-alcoholic potash, and, after dilution with water, the nitrile was removed by extraction with ether; on acidifying the alkaline solution the acid was obtained, and was distilled under 12 mm. pressure, when it passed over as a colourless oil, boiling at 144—148°, and possessing the odour of a fatty acid:

0.1195 gave 0.3110 CO_2 and 0.0999 H_2O . $C = 71.1$; $H = 9.3$

$C_{10}H_{16}O_2$ requires $C = 71.4$; $H = 9.5$ per cent.

Its basicity was controlled by titrating with $N/10$ -sodium hydroxide:

0.2146 neutralised 0.0508 $NaOH$, whereas the same weight of a monobasic acid, $C_{10}H_{16}O_2$, requires 0.0511 $NaOH$.

The above acid is doubtless identical with that obtained by Wallach and Evans (*Annalen*, 1908, 360, 51), who give the boiling point 155—157°/17 mm.

α -Phenyl- Δ^1 -cyclohexene-1-acetonitrile,



This substance was prepared as follows: Phenylacetonitrile (12 grams) was mixed with a solution of sodium (2.3 grams) in ethyl alcohol, and, after cooling, cyclohexanone (10 grams) was added. The product was heated for fifteen minutes on the water-bath, and the solution became somewhat yellow in colour. It was then cooled, diluted with water, acidified, and the precipitated oil extracted with ether. The ethereal solution was washed with water and dilute sodium carbonate, dried, and evaporated. On distillation of the residue, a colourless oil was obtained, which distilled at 176°/10 mm., and possessed a pleasant ethereal odour:

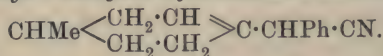
0.1160 gave 0.3618 CO₂ and 0.0825 H₂O. C = 85.1; H = 7.9.

C₁₄H₁₅N requires C = 85.3; H = 7.6 per cent.

A portion of the distillate, which was too small to investigate, crystallised after some time.

The hydrolysis of this nitrile was attempted with alcoholic sulphuric acid, and also with alkalis, but the result in each case was the decomposition of the molecule with the formation of phenylacetic acid and cyclohexanone.

α-Phenyl-1-methyl-Δ³-cyclohexene-4-acetonitrile,



The preparation of this nitrile is analogous to that which has been described above. The oil on distillation passed over as a colourless liquid at 191°/13 mm., and possessed a faint but pleasant odour of nitrile:

0.1133 gave 0.3533 CO₂ and 0.0849 H₂O. C = 85.0; H = 8.3.

0.1263 „ 7.6 c.c. N₂ at 18° and 752 mm. N = 6.8.

C₁₅H₁₇N requires C = 85.3; H = 8.1; N = 6.6 per cent.

We wish to extend our thanks to Prof. W. H. Perkin for the interest he has manifested in the progress of this investigation.

THE UNIVERSITY,
MANCHESTER.

LIV.—*The Direct Union of Carbon and Hydrogen at High Temperatures. Part II.*

By JOHN NORMAN PRING.

THE question of the direct union of carbon and hydrogen, which formed the subject of a previous paper by the author in conjunction with R. S. Hutton (Trans., 1906, **89**, 1591), has recently received a good deal of attention. In the paper just cited, the synthesis of acetylene at relatively very low temperatures (from 1850° upwards) was established, but the investigation of the formation of methane at lower temperatures gave less decisive results, and all that could be said was that the reactivity of the carbon diminished with continued use, and that the presence of impurities increased the methane formation, probably by catalysis.

As the temperature was raised in approaching the acetylene stage, and above this temperature, an increase in the methane was observed, which may be explained by the decomposition of the acetylene and the well-known greater stability of methane.

The present work is intended, by still greater precaution in the purification of the reacting substances, and by approaching the equilibrium stage from the opposite side, to clear up some of the outstanding points of uncertainty, and particularly to ascertain the equilibrium values of methane in the system methane, hydrogen, and carbon over a large range of temperatures.

Bone and Jerdan (*Trans.*, 1897, **71**, 41; 1901, **79**, 1042) first announced the possibility of obtaining methane by the direct union of carbon and hydrogen at 1200°. The percentage of methane obtained in these experiments varied from 0.7 to 1.4, mean 1.26.

Berthelot (*Ann. Chim. Phys.*, 1905, [viii], **6**, 183) disputed the above results, and emphatically expressed his belief that no hydrocarbons are produced at 1200—1350°, provided that the reacting materials are subjected to an exhaustive purification.

Mayer and Altmayer (*Ber.*, 1907, **40**, 2134) investigated the methane equilibrium in the system methane, hydrogen, and carbon. Hydrogen was allowed to react with carbon, to which nickel was added to serve as a catalyst. Experiments on the direct formation and on the decomposition of methane were made between the temperatures 470° and 620°.

In the thermodynamical equation:

$$KT = -18507 + 5.9934 T \log T + 0.002936 T^2 + RT \log \frac{\text{CH}_4}{(\text{H}_2)^2},$$

as expressed by Haber, which gives the equilibrium ratio of methane to hydrogen at all temperatures, the constant K was found by Mayer and Altmayer to be 21.1. At 1200° (1473° abs.) this gives the value of 0.07 per cent. for methane.

The experimental work is not, however, at all conclusive, as analyses of the gases show amounts of nitrogen varying from 2 to 20 per cent., and the percentages of carbon monoxide are not published.

H. von Wartenberg (*Zeitsch. anorg. Chem.*, 1909, **52**, 299) investigated the cyanogen, hydrocyanic acid, and acetylene equilibria, but his experiments were carried out in a very rough manner, and he only extended the work to exceedingly low concentrations of acetylene. In criticising the work of the present author and Hutton, Wartenberg overlooks the fact of the decomposition of acetylene into methane, and points out the anomaly of acetylene which is endothermic and methane which is exothermic both increasing in quantity at the higher temperatures.

Bone and Coward (Trans., 1908, **93**, 1975) extended the earlier work of Bone and Jerdan, and claimed finally to have proved the direct union of carbon and hydrogen by the conversion of given weights of carbon into a practically quantitative yield of methane. Although it seems probable that the conclusions of Bone and Jerdan and Bone and Coward, that carbon unites directly with hydrogen to form methane, will be upheld, the fact that in their experiments the carbon was always in contact either with some known catalyst or with porcelain, which, by reduction, might yield a catalytically active compound, fully justifies the further investigation of this reaction, which, moreover, is essential before concluding that direct union occurs.

For these reasons it was thought desirable, in the course of the present investigation, to adopt means to carry out the purification of the carbon to the highest possible degree, and to use hydrogen in the purest and driest condition, so as to eliminate any possible complication through the presence of carbon monoxide and nitrogen. It was also thought it would be of interest to investigate different kinds of carbon in their behaviour towards hydrogen. The varieties studied were retort carbon, sugar-charcoal, and graphite.

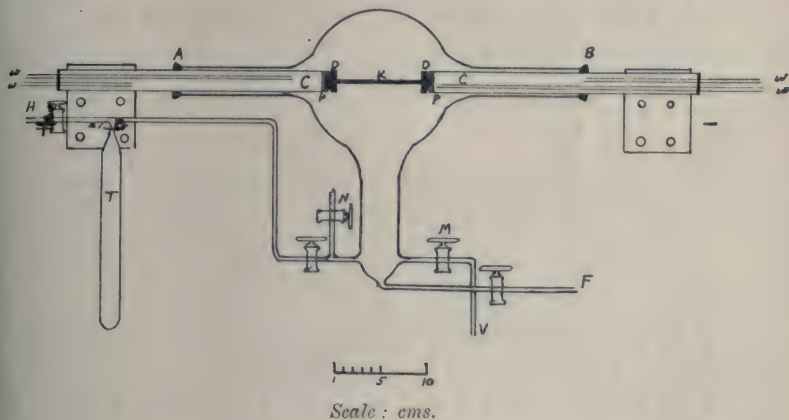
The method employed was similar to that used in the earlier work (Pring and Hutton, *loc. cit.*), and consisted in the use of a rod of carbon, or of a graphite tube provided with a narrow slit along the top, and inside which could be placed the variety of carbon it was desired to study. These rods or tubes, which could be heated to any desired temperature by the passage of an electric current, were suitably mounted at a considerable distance from the glass walls of the containing vessel, and all contact of the heated parts of the carbon with any substance but the surrounding hydrogen was avoided.

The temperature of the carbon rods, in this manner, is surprisingly uniform, and can be readily estimated by means of a Wanner optical pyrometer.

A tubular glass flask, of $2\frac{1}{4}$ litres capacity, formed the reaction vessel, as shown in Fig. 1. The tubes *CC*, of brass or copper, were stopped at *PP* with brass plugs by brazing. Graphite pieces *DD* were inserted by mere contact in holes bored in the brass plugs, and the graphite supported the carbon rod or graphite tube *K*. A slow circulation of water through the metal tubes by means of the tubes *ww* during the heating of the rods sufficed to keep the former quite cold. No visible heating of the graphite end pieces was ever observed, whilst the temperature of the rod was uniform to within 2 or 3 mm. from these supports. The metal tubes were fitted gas-tight at *A* and *B* by soft wax, which was occasionally

coated over with a solution of collodion in alcohol. These wax lutings allow the tubes a little play during the expansion of the rod by heat and remain perfectly gas-tight under these conditions, even when the flask is completely evacuated. The leak of air into the vessel seldom corresponded with more than 1 mm. when the flask was kept for one day under 1 cm. pressure. A charcoal tube was fitted at *T*, which could be cooled by liquid air, and thus complete the exhaustion of the vessel. Before each series of experiments, this exhaustion was allowed to proceed for a few hours, and the rod kept at a temperature of about 1500° in order to dry the inside walls of the vessel as completely as possible and remove any occluded gas or final impurity from the carbon. The outlet tube *H* was to enable a

FIG. 1.



preliminary partial exhaustion of the apparatus by a water pump, and the outlet *F* led to a mercury gauge and to a Töpler mercury pump, where a more complete exhaustion could be effected or samples of gas withdrawn from the vessel for analysis. The hydrogen used in these experiments was generated by the electrolysis of baryta solution. The baryta was for this purpose recrystallised several times, and the electrolysis conducted in a large U-tube placed in a hot-water bath, a current of about 3 amperes being used. The hydrogen was then passed through a heated Jena combustion tube filled with copper gauze, a small heated tube filled with platinised asbestos, and then through a calcium chloride tube. Two methods were then at different times used for further purification of the gas.

A. After leaving the calcium chloride tube, the hydrogen was

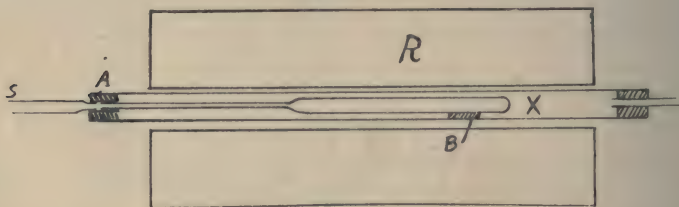
passed through a spiral glass tube, cooled on the outside by liquid air. The air in the drying tubes was first displaced by passing a current of hydrogen through for several hours, and allowing to escape through a side-tube, which dipped under mercury. The hydrogen was then admitted through the tap *M*, which could be carefully regulated, into the vacuous globe.

B. The gas was filtered through a specially constructed palladium tube, making use of the well-known permeability of this metal to hydrogen when slightly heated.

The tube was of the form shown in Fig. 2 at *X*, the total length being 30.5 cm., external diameter of wide part 5 mm., and of narrow part 2 mm., thickness of walls 0.5 mm., weight 14.2 grams. The tube was connected to the glass at *A* by means of rubber valve tubing, which was then covered with pressure tubing.

The palladium was encased in a Jena glass tube, actual contact with the glass being avoided by a palladium bridge at *B*. The

FIG. 2.



glass tube was surrounded by an electrical wire resistance furnace *R*, whereby a temperature of 350–400° could be conveniently maintained. The outlet tube *S* was sealed on to the tube *V* (Fig. 1). By opening the tap *M* (Fig. 1), the palladium tube could be evacuated together with the flask, and, on warming, perfectly pure hydrogen diffused through and gradually filled the vessel. The rate of diffusion varied, of course, with the pressure inside the flask. With the palladium tube at 400°, when the vessel was vacuous, about 20 c.c., and with a pressure of 60 cm. about 5 c.c., entered per minute. It was never necessary to fill the vessel entirely, as the subsequent heating of the rod expanded the gas to atmosphere pressure.

Temperature Readings.

It was found by comparison with a thermo-element (H. C. Greenwood, Trans., 1908, **93**, 1486; *Proc. Roy. Soc.*, 1909, **82**, A, 402) that the particular pyrometer used is accurate within 20° at 1250° when sighted on to the outside of the carbon rod, and that at

1550°, 1670°, and 2000° there is not a departure of more than 15° for "black body" radiation. Consequently, the only error of any magnitude which could arise at these temperatures would be due to departure from "black body" radiation, and this deviation in the case of carbon is known to be small. In the experiments described below, the pyrometer was calibrated against a thermoelement at 1200°, and then frequently checked by means of an amyl acetate lamp.

Analysis of Gas.

The estimation of the small quantities of methane in the previous work (Pring and Hutton, *loc. cit.*), which was effected in a Sodeau apparatus, without a preliminary condensation of the hydrogen, was a matter of some difficulty on account of the tendency to form oxides of nitrogen on exploding the gas with excess of oxygen.

The presence of acetylene was ascertained qualitatively by the formation of cuprous acetylide, but in the quantitative estimation, by the use of bromine or fuming sulphuric acid, no means were adopted to distinguish between the acetylene and ethylene or any other unsaturated hydrocarbon.

In the work now described, a condensation of the hydrogen was usually first made by means of palladium foil in cases where no unsaturated hydrocarbons were present. In this way, 1000 to 1500 c.c. of the resulting gases were condensed to 50—100 c.c., and thus an accuracy of from ten- to thirty-fold in the methane estimation was obtained. Samples of gas which contained unsaturated hydrocarbons, in addition to methane, were not condensed by palladium, but were analysed as follows: The gas was first treated with a solution of ammoniacal silver chloride to remove acetylene. Two separate lots of this reagent were used, the last being freshly prepared, to ensure complete removal of this gas. A treatment with bromine or fuming sulphuric acid, followed by potassium hydroxide solution, was then carried out, to remove ethylene. The carbon monoxide was then removed by two treatments with ammoniacal cuprous chloride solution, and the methane estimated by exploding with an excess of oxygen and measuring the carbon dioxide.

Purification of Carbon.

The method employed by Bone and Jerdan and Bone and Coward (*loc. cit.*) for purifying the carbon consisted in igniting the finely divided substance for several days in a stream of chlorine, followed by hydrogen, at a temperature of 1100—1200°. The disadvantage

of this method lies in the improbability of ever being able to remove the last traces of combined hydrogen, and the serious contamination which must result from contact with the containing vessel during the long period necessary for the treatment.

The methods adopted in the present investigation were as follows.

A. In the cases where amorphous carbon rods, usually of 0.4 cm. diameter and 10 cm. long (retort carbon), were used, these were placed in a carbon tube furnace and treated for two to three hours with a current of chlorine at about 1500° , and then for about fifteen minutes with a current of nitrogen, and finally for two to three hours with a current of hydrogen. The carbon tube used for this furnace was 28 cm. long and 2 cm. external diameter. Electrical connexions were made at the end by graphite rectangular bars, and a current of 160 amperes at 11 volts was found to produce a temperature of about 1550° when charcoal was used as packing around the tube.

An analysis made of a rod after this purification showed the presence of less than 0.10 per cent. of hydrogen and 0.05 per cent. of ash. After this treatment, the rod was mounted in the glass reaction vessel, being supported by the graphite end-pieces. It was here raised to a temperature of about 1500° by the passage of an electric current while the vessel was kept at a high vacuum by means of charcoal cooled by liquid air. In some experiments a measurement was made, by means of a McLeod gauge, of the pressure inside the vessel under these conditions, and was found to vary from 0.01 to 0.10 mm. It was found possible to maintain this low pressure for an indefinite period. The carbon rod, which was heated for an interval of from one to five hours, received in this way a further purification, while an effective drying of the inside of the vessel was at the same time ensured.

In addition to the above treatment, great importance is attached to the fact that the same rod was used continuously throughout a large number of experiments, after each of which the heating in vacuum was again repeated for a short time, and only the pure hydrogen was allowed to enter the vessel after each evacuation.

B. In the case of experiments with sugar-charcoal, the procedure consisted in gradually igniting sugar to a bright red heat, reducing the carbon to a fine powder, placing in a graphite boat, and treating this in the carbon tube furnace alternately with chlorine, nitrogen, and hydrogen, as described above for the rods. A tube was prepared from Acheson graphite, 9.5 cm. long, 0.95 cm. external, and 0.6 cm. internal diameter, and provided with a narrow longitudinal slit. This was subjected to a prolonged purification treatment, and then filled with the purified charcoal and mounted

in the glass vessel in the manner employed with the rods. In one series of experiments the carbon used was purified with even more rigour, by repeating the alternate treatment with chlorine, nitrogen, and hydrogen, at 1550° for six times over a total period of six hours.

A disadvantage found with these tubes is that, unlike the case of the thinner carbon rods, the temperature is only uniform over a central region of about two-thirds of the tube, and from here it gradually falls off to the cooled supports. At higher temperatures, however, this uniform zone extends over a somewhat greater length.

Another inconvenience with this method is that while the temperature of the tube is being raised, the finely divided carbon shows a curious tendency to disperse and be expelled from the aperture, even when this is very small. This scattering is much more marked when the heating is done in a vacuum, and in all cases necessitates a very gradual raising of the temperature.

C. For examining the reaction with graphite, the tube employed in the above experiments was used empty, having been purified by prolonged treatment with chlorine and hydrogen.

The procedure in an experiment was as follows. After the preliminary heating of the purified carbon in the evacuated reaction vessel, pure hydrogen was admitted through the tap *M* (Fig. 1). The pressure of hydrogen could be measured by means of the mercury gauge connected to *F*, which also led to the pump *L*. The mercury gauge also served as an outlet for the gas during its expansion through the heating of the carbon. During the experiment the current employed was kept constant, and temperature readings were taken at frequent intervals by the Wanner optical pyrometer. At the end of each experiment the gas was removed by a Töpler pump and transferred to a graduated gas holder containing glycerol and water, and after measurement was condensed by palladium foil. Sixty grams of this foil, cut into small strips, were, for this purpose, placed in a 300 c.c. flask provided with a wide ground-glass stopper and a side-tube with a ground joint and mercury seal. The flask was exhausted by a Töpler pump, and the gas from the holder then allowed to enter. The flask was heated by a water-bath to $80\text{--}100^{\circ}$, when absorption of the hydrogen was very rapid if the amount of carbon monoxide present was below 0.01 per cent. The residual gas was removed by the pump, measured over mercury, and analysed.

Tabulated List of Results.

Values for the methane, given to two places of decimals, denote that the analysis has been made on the uncondensed gas, whilst

the methane in the gas condensed by palladium has been estimated to three places. The same carbon was used throughout each series without, in any way, dismantling the apparatus.

Part 1.—Reactions Examined in Presence of Carbon Monoxide.

A. Sugar-charcoal in graphite tube.

Series 1.—Sample purified by heating once in chlorine, nitrogen, and hydrogen alternately for one hour at 1550° , and then for half an hour in a vacuum, at 1200° , in the reaction vessel:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).		
			CO.	CH ₄ .	N ₂ .
1	1200—1250°	2	0.70	0.29	0.15
2	1345	1½	0.66	0.247	—

Series 2.—Sample of sugar-charcoal purified by heating alternately in chlorine, nitrogen, and hydrogen six times for six hours at 1550° , and then in a vacuum for half an hour before each experiment:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).		
			CO.	CH ₄ .	N ₂ .
1	1250°	1½	0.87	0.400	—
2	1250	1½	0.6	0.4	0.3
3	1250	2	0.35	0.279	—
4	1250—1300	1	0.36	0.198	—
5	1250	½	0.87	0.24	0.20
—	—	3	0.97	0.324	—
6	1500	1½	0.70	0.18	—

The above series clearly shows the diminution in the amount of methane formed after the first few times of use.

Series 3.—Sample of sugar-charcoal purified by heating five times alternately in chlorine, nitrogen, and hydrogen for five hours, and then in a vacuum as above:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).	
			CO.	CH ₄ .
1	1230—1270°	1½	0.8	0.106
2	1615	1	1.8	0.143
3	1250	2	0.65	0.196

The above series was conducted with the view of ascertaining if the heating of the carbon to about 1600° would cause any marked diminution in the reactivity.

B. Experiments with graphite:

Order of experiment.	Temperature.	Time in hours.	Product (percentage).	
			CO.	CH ₄ .
1	1250°	1½	0·15	0·143
6	1250	1½	0·01	0·046
5	1250	4	0·13	0·232
7	1250	4	0·25	0·252
3	1325	1½	0·18	0·170
4	1520	1½	1·3	0·172
5	1720	1½	2·0	0·246

*Part 2.—Reactions Conducted with Very Low Concentrations of Carbon Monoxide.**Series 1.—Retort carbon.*

Amorphous carbon rod purified by heating alternately in chlorine, nitrogen, and hydrogen for two hours at 1550°, and then in the reaction vessel in a vacuum at 1425° for two hours:

Order of experiment.	Temperature.	Time.	Product (percentage).			
			CO.	CH ₄ .	C ₂ H ₂ .	C ₂ H ₄ .
4	1100°	3½ hours	0·006	0·123	—	—
6	1100	13 "	0·012	{ 0·308	—	—
1	1150	2½ "	0·3	{ 0·312	—	—
7	1200	50 mins.	<0·01	0·238	—	—
5	1200	5 hours	0·01	0·150	—	—
18	1200	11 "	0·165	—	—	—
13	1200	22 "	<0·005	0·334	—	—
2	1300	1½ "	0·01	0·342	—	—
3	1300	4 "	0·15	0·160	—	—
8	1300	4 "	0·01	0·220	—	—
8	1400	2 "	0·010	0·178	—	—
9	1500	2 "	0·04	0·168	—	—
11	1600	35 mins.	0·001	0·210	—	—
10	1600	1¾ hours	0·02	0·240	—	—
12	1725	1 hour	<0·002	0·354	—	—
14	1770	15 mins.	0·32	0·402	—	—
15	1830	12 "	0·15	0·530	nil	—
16	1850	1 hour	0·05	0·597	trace	—
17	1950	30 mins.	0·44	0·86	0·20	0·22
19	2055*	10 "	0·33	1·13	1·30	0·97

* Rod broke and arced for about three seconds at end.

Series 2.—Amorphous carbon rod, heated as last one.

1	1570°	1 hour	0·160	0·154	nil	nil
2	1620	80 mins.	0·087	0·181	"	"
3	2080	15 "	0·35	1·08	0·45	0·45
4*	2180	11 "	0·10	2·18	1·80	1·72

* Rod arced for about three seconds at end.

Part 3.—Decomposition of Acetylene and Methane in Presence of an Excess of Hydrogen at High Temperatures.

Experiments on the decomposition of these hydrocarbons were undertaken to attempt to decide to what extent methane might arise at the higher temperatures as a secondary action from the decomposition of acetylene, to measure its stability at these temperatures, and, if possible, to find the final equilibrium value of methane from the other side.

Acetylene was for this purpose prepared by dropping ethylene dibromide into hot alcoholic potash, washing the gas with alcohol, and collecting over water.

About 5 litres of this were condensed by liquid air and then allowed to evaporate, the middle portion being passed into a holder of about 200 c.c. over mercury. From here it could be admitted into the reaction vessel through the tap *N*, the connecting tube having first been evacuated, together with the vessel. Methane was prepared by decomposing commercial aluminium carbide with dilute hydrochloric acid, washing the gas well with ammoniacal cuprous chloride to remove acetylene and hydrogen sulphide, and then liquefying the methane, vaporising, and collecting the middle fraction.

Small percentages of acetylene or methane could in this way be admitted into the reaction vessel, which was then filled with hydrogen. An amorphous carbon rod was used. Samples of gas were withdrawn from the reaction vessel before and after each experiment. In some cases condensation with palladium was resorted to. The results are tabulated below:

Ex- periment.	Temperature.	Time.	Composition of gas.			
			CO.	CH ₄ .	C ₂ H ₂ .	C ₂ H ₄ .
1	1480°	0	—	—	0·6	—
		1 hour	0·15	0·32	nil	trace
		2 hours	0·2	0·25	„	„
		4½ „	0·25	0·25	„	„
2	1200°	0	—	—	3·50	—
		1½ hours	0·27	4·20	0·50	0·85
		5½ „	0·41	1·41	nil	0·35
		8 „	0·48	1·00	„	0·35
3	1775°	0	—	—	20·2	—
		10 mins.	0·08	5·93	5·02	1·13
		1 hour	0·09	0·77	nil	nil
4	1200°	0	—	6·00	—	—
		25 hours	0·073	4·63	—	—
5	1580° to 1620°	0	—	5·0	—	—
		2 hours	0·05	1·75	—	—
6	1200°	0	—	6·73	—	—
		2 hours	0·25	5·47	—	—

Experiment in which 5 per cent. of carbon monoxide was added, to study its effect on the decomposition of methane:

7	1200°	0	5.0	6.5	—	—
		3 hours	4.2	5.92	—	—
		6½ „	3.72	5.95	—	—

Part IV.—Amorphous Carbon Rod with a Deposit of Platinum on Surface to Assist the Reaction Catalytically.

This rod was purified in chlorine, nitrogen, and hydrogen at the same time as the previous ones, and was coated with a thin deposit of platinum by electro-deposition, and then heated in the reaction vessel in a vacuum at 1300° for half an hour. Pure hydrogen was then admitted, and the experiment conducted as usual. In the experiments in column B a small percentage of methane was admitted to find the equilibrium from the decomposition.

A.

Order of experiment.	Temperature.	Time.	Product (percentage).	
			CO.	CH ₄ .
1	about 1050°	1½ hours	0.052	0.866
2	„ 1100	6½ „	0.007	0.690
8	1200	2 „	0.011	0.540
3	about 1300	30 mins.	0.014	0.340
6	1500	45 „	nil	0.297

B.

Decomposition of methane with same rod.

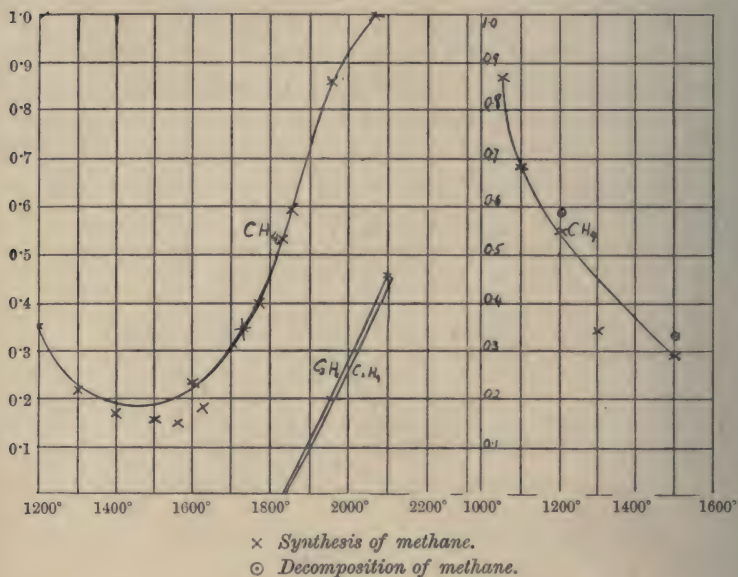
4	1175—1200°	0	—	2.31
		4 hours	0.006	1.14
5	1200	0	—	1.95
		12 „	0.003	0.594
7	1500	0	—	3.2
		2 „	1.03	0.330

Conclusions.

The experiments described above clearly show that pure carbon combines directly with pure hydrogen at all temperatures above 1100°. At 1200° the velocity of the reaction is so slow in the absence of any catalyst that the estimation of the exact equilibrium value of methane is somewhat uncertain. An experiment extending over twenty-two hours at 1200° seemed, however, to yield the limiting value of 0.35 per cent. of methane, although this could not be confirmed by approaching the equilibrium from the other side, as the decomposition of small amounts of methane by pure carbon at 1200° proceeds even more slowly than the synthetic reaction.

At 1500° an equilibrium value of 0.17 per cent. of methane appeared to be approached within about two hours, although even at this temperature the decomposition of methane was too slow to serve for the evaluation of the equilibrium quantity. More definite equilibrium values were obtained by using carbon which contained a surface deposit of platinum. In this case, in experiments at temperatures between 1050° and 1500° , the reaction was very much accelerated, and the same percentage of methane was finally obtained whether its formation or its decomposition was

Synthesis of hydrocarbons from pure amorphous carbon. Maximum amounts obtained. *Methane equilibrium with platinum coated carbon.*



investigated. The amount formed was 0.55 per cent. at 1200° , and 0.30 per cent. at 1500° .

Above 1550° the percentage of methane began to rise with the temperature. These increased quantities of methane do not, at these temperatures, necessarily represent equilibrium values, but probably arise from the decomposition of acetylene, although the amount of the latter gas present was too small to be detected below 1850° .

Experiments on the decomposition of hydrocarbons showed that acetylene changes quickly to methane and ethylene above 1500° , and that the methane formed is comparatively stable. This behaviour is similar to the decomposition which hydrocarbons

undergo at lower temperatures (Bone and Coward, Trans., 1908, **93**, 1197).

In the decomposition of acetylene at 1200—1400°, ethylene was also formed, and found to persist; consequently, this appears to preclude the possibility of the methane arising secondarily in the experiments at these temperatures, as, in these cases, no trace of ethylene was found in the gas.

Graphite and sugar-charcoal showed a similar behaviour to amorphous retort carbon in its reactivity with hydrogen.

The presence of carbon monoxide seems to have no effect on the final equilibrium in the synthesis or decomposition of methane at any temperature employed, or on the velocity of the reaction. The synthesis of acetylene could not be taken to the equilibrium stage, as with methane, in the form of apparatus used. Acetylene, being endothermic, is stable in larger amounts the higher the temperature, and would consequently undergo some decomposition in passing away from the heated carbon through the intermediate zones of temperature of the outside layers of gas.

The equilibrium values obtained in the above work probably refer to systems of different concentrations than the surrounding gases, on account of a probable condensation of gas on the surface of the carbon or catalyst. This problem is now being investigated by the use of high gaseous pressures and the examination of the effect of catalysts other than platinum.

In conclusion, I wish to express my indebtedness to Professor E. Rutherford for the facilities he has extended for conducting this research, and to Dr. R. S. Hutton for suggesting the work, and for his continued interest and assistance during its progress.

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LV.—*The Colour and Constitution of Azo-compounds.* *Part V.*

By JOHN THEODORE HEWITT and FERDINAND BERNARD THOLE.

DURING the progress of some work on the relationships existing between the constitution and selective absorption of certain polyazo-compounds, the authors of the present communication were much struck with the great colour change which takes place on diazotising

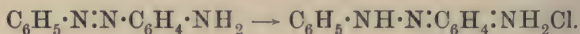
aminoazobenzene in hydrochloric acid solution. As is well known, azobenzene and aminoazobenzene both dissolve in alcohol, with a shade which is yellow in dilute solution, the head of the band of slowest oscillation, but little persistence, lying at about 2200 oscillation frequency in the case of azobenzene (Hartley, *Trans.*, 1887, **51**, 152; Baly and Tuck, *Trans.*, 1906, **89**, 985; Hantzsch, *Ber.*, 1909, **42**, 2132), and apparently at about the same point with the amino-derivative (compare Landauer, *Ber.*, 1881, **14**, 391, and C. Graebe, *Zeitsch. physikal. Chem.*, 1892, **10**, 689). The best marked and most persistent band given by alcoholic solutions of azobenzene has its head at an oscillation frequency of about 3200.

Similar observations have been made in the case of dimethyl-aminoazobenzene (2430, Hantzsch, *loc. cit.*, p. 2133), *p*-aminobenzeneazophenol (2600), and *p*-dimethylaminobenzeneazophenol (2400, Hewitt and Thomas, *Trans.*, 1909, **95**, 1297).

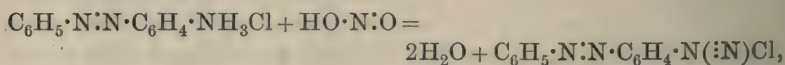
In all cases, however, where an amino-group occupies a para-position with respect to the azo-group, the formation of a monacid salt by the addition of dilute hydrochloric acid in sufficient quantity conditions a change in colour to red, the oscillation frequencies of the heads of the persistent band of longest wave-length lying at about the same point for the compounds enumerated; this is shown in the following table:

<i>p</i> -Aminoazobenzene	2000 (see Fig. 1)
<i>p</i> -Dimethylaminoazobenzene	1900 (Hantzsch)
<i>p</i> -Aminobenzeneazophenol	1800 (Hewitt and Thomas)
<i>p</i> -Dimethylaminobenzeneazophenol ...	1800 " " "

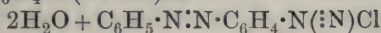
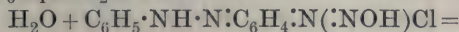
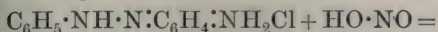
This change, which corresponds with that observed on acidifying a solution of methyl-orange, is now generally explained by supposing the hydrochlorides to be derived from the equivalent quinonoid form:



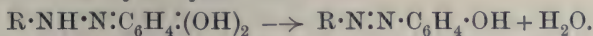
The possibility of a certain small amount of amino-aromatic salt being also present in solutions is not completely negatived, since one may adduce in support of such a proposition the fact that Hantzsch has in some cases isolated yellow salts of aminoazo-compounds, and has also obtained a tribromo-derivative of aminoazobenzene by the direct action of the halogen in glacial acetic acid solution (*Ber.*, 1908, **41**, 1171, 1187, 2435); whilst, further, there is the well-known aptitude for diazotisation of the aminoazo-compounds. In the last case one is inclined to formulate the reaction as taking place according to the scheme:



although reaction in the sense:



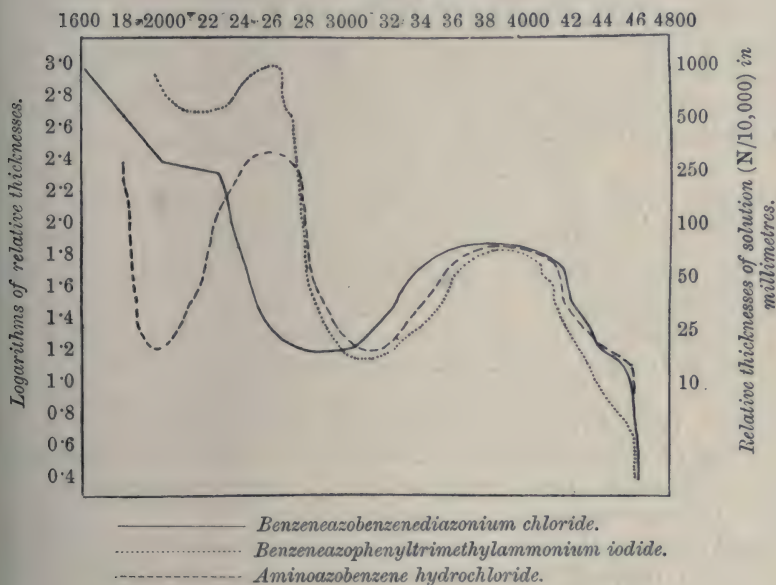
does not seem so improbable when one considers the easy way in which the quinonoid hydrates of azophenols lose water, passing directly into the hydroxyazo-form:



It is certainly highly improbable that the diazonium chlorides possess a similar structure to the salts of the parent aminoazo-

FIG. 1.

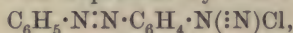
Oscillation frequencies.



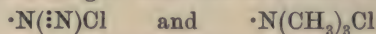
compounds, for on adding nitrite to the bluish-red solutions of the latter, the colour changes to an orange, which to the unassisted eye appears rather more red in shade than that of the free aminoazo-compounds or of azobenzene itself. In these circumstances it appeared very desirable to examine the absorption spectra, and for this purpose we have compared benzeneazobenzenediazonium chloride with the hydrochloride of aminoazobenzene on the one hand, and with benzeneazophenyltrimethylammonium iodide on the other. Comparison with other para-derivatives of azobenzene is also possible, and, as will be seen from the curve given in Fig. 1, benzene-

azobenzenediazonium chloride gives a curve which resembles somewhat closely that given by benzeneazophenol (Tuck, Trans., 1907, **91**, 450). The head of the absorption band for benzeneazophenol lies at an oscillation frequency of about 3000, whilst for the diazonium salt examined it is about 2950. Further, both of these substances show an extension of the band towards the red end of the spectrum; a similar extension has also been observed with certain aminoazophenols by Hewitt and Thomas (*loc. cit.*).

On the same diagram will be found the curves for the absorption spectra furnished by the hydrochloride of aminoazobenzene and by benzeneazophenyltrimethylammonium iodide. The first of these substances is almost without doubt of quinonoid structure, and its absorption, which closely resembles that of the hydrochlorides of dimethylaminoazobenzene and its hydroxy- and methoxy-derivatives, is absolutely different from that of the other two compounds, which do not, however, agree as closely between themselves as might have been expected for substances possessing similar structures. It therefore remains an open question whether the constitution of the diazonium salt is to be expressed by the formula:



although it might be urged that the difference in the groups



might account for the comparatively minor differences in the absorption spectra.

Comparison of the absorption spectra of phenol (Baly and Ewbank, Trans., 1905, **87**, 1351) and benzenediazonium salts would have been interesting, but since, according to Dobbie and Tinkler (Trans., 1905, **87**, 273), the latter give absorption spectra similar to those of dilute solutions of the unstable diazotates, a reference to the curve given in the latter case by these authors shows that very little aid can be expected.

For the purposes of this work, aminoazobenzene was acetylated, the acetyl derivative recrystallised until of constant melting point, and hydrolysed. In examining its acid-alcoholic solution, hydrochloric acid was added in such amount as not to produce any further deepening of the red shade.

The benzeneazophenyltrimethylammonium iodide was prepared by heating benzeneazodimethylaniline with methyl alcohol and methyl iodide to 100° after keeping the mixture for eighteen hours in the cold, and reaction was already practically complete. The product was finally recrystallised from a large quantity of boiling water.

Benzeneazobenzenediazonium Chloride.—The isolation of the solid diazonium salt was effected by suspending 4.7 grams of aminoazo-

benzene hydrochloride in 150 c.c. of alcohol (96 per cent.), and adding 2.4 grams of amyl nitrite diluted with 10 c.c. alcohol. After fifteen minutes' stirring, any small solid residue was removed by filtration and the diazonium chloride precipitated by ether, collected, washed with ether, and dried over sulphuric acid. The salmon-coloured powder obtained in this way proved, under the microscope, to consist of a mass of small but well-defined prisms:

0.5506 gave 0.3211 AgCl. $\text{Cl} = 14.4$.

$\text{C}_{12}\text{H}_9\text{N}_4\text{Cl}$ requires $\text{Cl} = 14.5$ per cent.

The salt dissolves in alcohol and water, showing considerable stability even in alcoholic solution. The absorption spectra were observed with freshly prepared alcoholic solutions, but even after keeping overnight at the ordinary temperature a large amount of the diazonium salt was found to be still undecomposed. On heating, the salt decomposes comparatively gently; no detonation has been observed, whilst the dry salt may be kept for months without appreciable decomposition, still dissolving in water and coupling with the usual azo-components. An aqueous solution reacts, however, immediately with potassium iodide, giving *p*-iodobenzene.

Platinichloride.—This salt was prepared by precipitating an aqueous solution of the chloride with excess of chloroplatinic acid; after washing and drying it formed a salmon-coloured powder. This salt also shows considerable stability, and decomposes in a gentle manner when heated:

0.3228 gave 0.0768 Pt. $\text{Pt} = 23.8$.

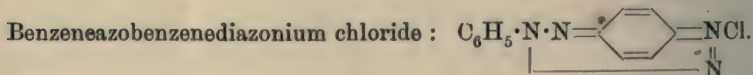
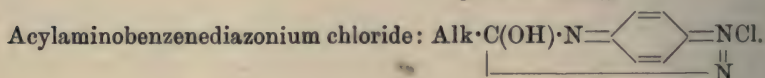
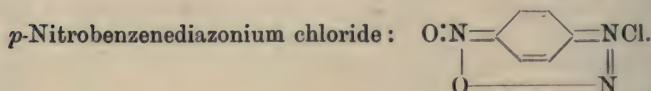
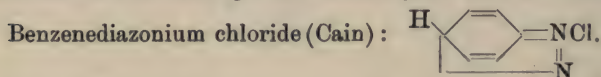
$(\text{C}_{12}\text{H}_9\text{N}_4)_2\text{PtCl}_6$ requires $\text{Pt} = 23.6$ per cent.

No *ferrichloride* has been obtained, but solutions of the chloride yield a yellow precipitate with potassium dichromate. The salt, presumably *benzeneazobenzenediazonium dichromate*, was washed and dried, but on account of the character of the detonation which occurred on heating, an analysis was not carried out. Meldola (Trans., 1905, **87**, 4) has also prepared this salt, but did not analyse it owing to its explosive properties.

The absorption spectra are not such that the authors feel justified in drawing any rigid conclusion as to the constitution of the *benzeneazobenzenediazonium chloride*; it is, however, a very remarkable fact that the most stable diazonium salts are always those possessing a para-substituent, especially when the latter happens to be an unsaturated and negative group. Reference may be made to the cases of *p*-nitrobenzenediazonium chloride, the acetylaminobenzenediazonium chloride described by Meldola (Proc., 1899, **15**, 196; Trans., 1905, **87**, 1), and to the benzenesulphonyl-

aminoaryldiazonium salts of Morgan and his co-workers (Trans., 1905, **87**, 73, 921, 1302; 1906, **89**, 4; 1907, **91**, 1311, 1505, 1512; 1908, **93**, 602).

Morgan and Alcock (Trans., 1909, **95**, 1319) adopt a modification of Cain's formula (Trans., 1907, **91**, 1040) for the constitution of diazonium salts, but apparently do not attribute the stability conferred by negative para-substituents to any essential difference in constitution. If one follows Cain in ascribing to diazonium salts a hemiquinonoid structure, the possibility certainly arises that salts of the negatively substituted type may be fully quinonoid in structure, and their greater stability be thus accounted for:



Thus, whilst Cain represents the simple diazo-salts as analogues of the labile "chinols," the above representation of the negatively substituted compounds resembles the constitution attributed to the far more stable quinones.

Iodoazobenzene.—In connexion with the work described in this paper, iodoazobenzene was examined with a view to seeing if it was capable of iodonium salt formation. As amino- and hydroxyazobenzene readily yield quinonoid salts, so it is not impossible that the iodo-derivative may give corresponding salts containing tervalent iodine:



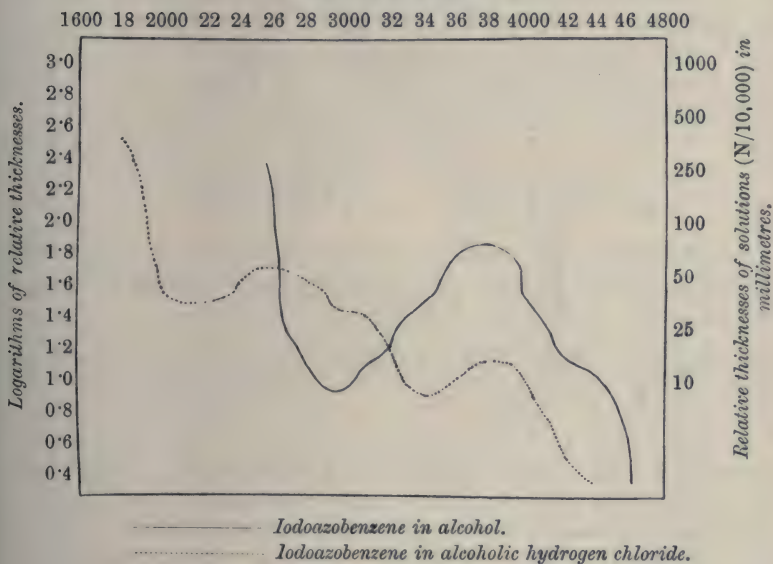
Since, however, azobenzene itself gives unstable salts with acids, it might be argued that any salts yielded by iodoazobenzene should be referred to the same type. It happens that azobenzene gives a different absorption in acid solution from that given by the monohydrochlorides of its amino- and hydroxy-derivatives; the absorption spectra of the two latter salts being comparable, although the head of the band of slowest frequency lies always more towards the red end of the spectrum in the case of the nitrogen compound.

When iodoazobenzene is dissolved in benzene and hydrogen

chloride led in, the colour darkens considerably, and separation of a certain amount of solid occurs. This method of preparing the salt, which gives such good results for hydroxyazo-compounds, is not very suitable for preparing salts of iodine derivatives, as the separation of solid matter is but slight. Nevertheless, a comparison of the absorption spectra of iodoazobenzene in alcohol alone and in alcoholic solution of hydrogen chloride (see Fig. 2) renders it quite probable that combination with hydrogen chloride occurs with formation

FIG. 2.

Oscillation frequencies. •



of an iodonium salt. In fact, when iodoazobenzene is moistened with benzene and exposed to gaseous hydrogen chloride, two molecules of the latter are absorbed, and a beautiful, nearly black, crystalline hydrochloride is produced.

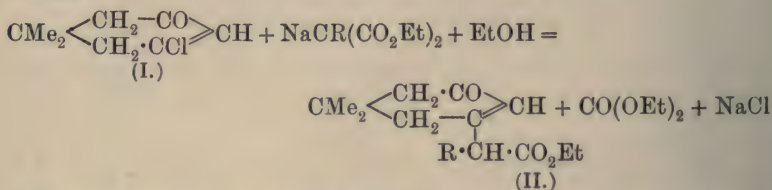
The authors acknowledge with thanks the aid afforded them by the Government Grant Committee of the Royal Society, by which the expenses of this research have been defrayed.

EAST LONDON COLLEGE.

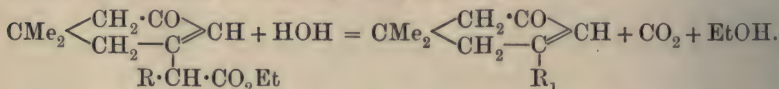
LVI.—*Action of Ethyl Cyanoacetate on 5-Chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one.*

By ARTHUR WILLIAM CROSSLEY and CHARLES GILLING (Salters' Fellow).

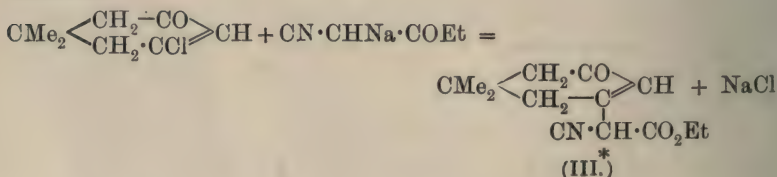
It has been previously shown (Trans., 1909, **95**, 19; Proc., 1909, **25**, 96) that 5-chloro-1:1-dimethyl- Δ^4 -cyclohexen-3-one (I) can be condensed with the sodium derivative of ethyl malonate (or substituted ethyl malonates) to form ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (II) with elimination of a molecule of ethyl carbonate:



These condensation products, on hydrolysis, give rise to a series of hydroaromatic ketones according to the following scheme, in which R=H, Me, or Et; R₁=Me, Et, or Pr:



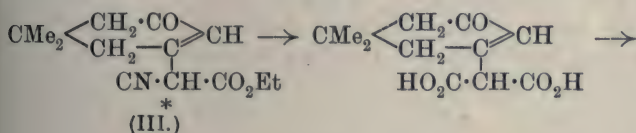
It was also mentioned (*loc. cit.*, Trans., p. 27) that a small quantity of a nitrogenous substance, melting at 141°, was always formed together with the condensation products of type II, due to the presence of ethyl cyanoacetate in the ethyl malonate employed. In continuance of the investigations on the chemical reactivity of the chlorine atom in chlorodimethylcyclohexenone, the latter substance was next condensed with the sodium derivative of ethyl cyanoacetate, when the substance melting at 141° is formed in about 75 per cent. of the theoretical quantity. It gives analytical numbers agreeing with the formula C₁₃H₁₇O₃N, and it was at first thought that the reaction should be formulated on similar lines to that taking place between ethyl malonate and chlorodimethylcyclohexenone:



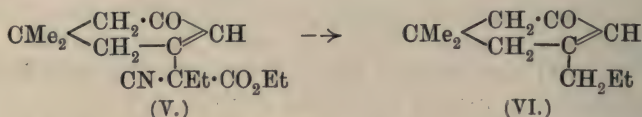
This assumes that in such reactions ethyl malonate and ethyl cyanoacetate behave as if they possessed similar constitutions. The chemical properties of the condensation product are not, however, in agreement with those which a substance having formula (III) should exhibit; for whereas ethyl dimethylcyclohexenoneacetate (II) is a perfectly neutral compound containing a ketonic group, as proved by the fact that it readily forms a semicarbazone, the solution of the ethyl cyanoacetate condensation product in aqueous alcohol has well-marked acidic properties, may be titrated against standard sodium hydroxide solution, and the neutral solution so obtained gives a green colour with ferric chloride. Moreover, it can be readily esterified with ethyl alcohol containing 5 per cent. of sulphuric acid, giving rise to a mixture of two ethyl derivatives, which can be separated by fractional crystallisation, and since they both possess the same general formula, the same molecular weight, and yield the same product on hydrolysis, it seems evident that they are stereoisomeric substances.

In a similar way two stereoisomeric methyl derivatives have been prepared.

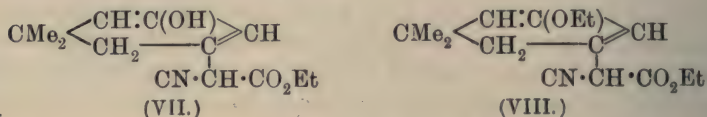
The substance melting at 141° cannot be hydrolysed by long-continued boiling with an alcoholic solution of potassium hydroxide, probably on account of the stability of the potassium salt formed, but when heated for an hour with concentrated hydrochloric acid, it is converted into 1:1:3-trimethyl- Δ^4 -cyclohexen-3-one (IV), a reaction which may be provisionally represented as follows:



derivative (V) would give on hydrolysis 3-propyl-1:1-dimethylcyclohexen-3-one (VI):

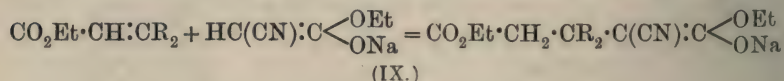


A simple explanation of the acidic properties is forthcoming if it be assumed that the original condensation product (III) undergoes tautomeric change, the ketonic oxygen becoming enolic, and giving rise to a substance of formula (VII), which on esterification (etherification) would yield (VIII).



In favour of this supposition is the fact that the substance melting at 141° forms condensation products with aniline and monomethylaniline. Whilst formula (III) admits of the formation of a compound with elimination, as water, of the ketonic oxygen with the two hydrogen atoms of the amino-group in the case of aniline, it does not admit of an analogous reaction in the case of methylaniline; but both reactions are easily explained by the adoption of formula (VII). It will be seen that the ethyl derivative (VIII) still shows the presence of a hydrogen atom attached to the carbon atom, situated between the cyanogen and carbethoxyl groups, and it should therefore be possible to introduce a second ethyl group into this position by the successive action of sodium and ethyl iodide. Although attempts were made to accomplish this end under a variety of conditions, they were always unsuccessful, and this, taken in conjunction with the fact that formula (VII) does not offer a ready explanation of the formation of two stereoisomeric modifications of the ethyl and methyl ethers, necessitates some other explanation of the reaction being sought.

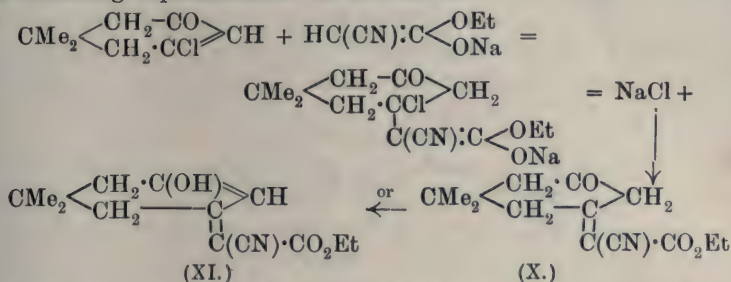
It has been proposed by J. F. Thorpe (Trans., 1900, 77, 925) that the formula which most adequately explains the behaviour of the sodium derivative of ethyl cyanoacetate is (IX), and the mechanism of its condensation with unsaturated substances is as follows:



where R may be either an alkyl group or hydrogen.

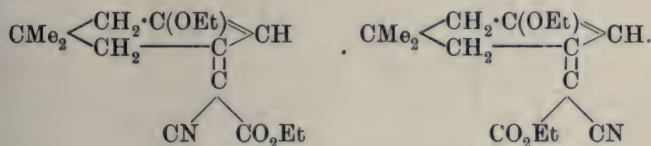
If, as kindly suggested to us by Dr. J. F. Thorpe, this formula

for ethyl cyanoacetate be applied in the reaction under discussion, the following representation is arrived at:



and the product would be *ethyl 3-hydroxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetate* (XI) (*ethyl 1:1-dimethylcyclohexan-3-onylidene-5-cyanoacetate*, X).

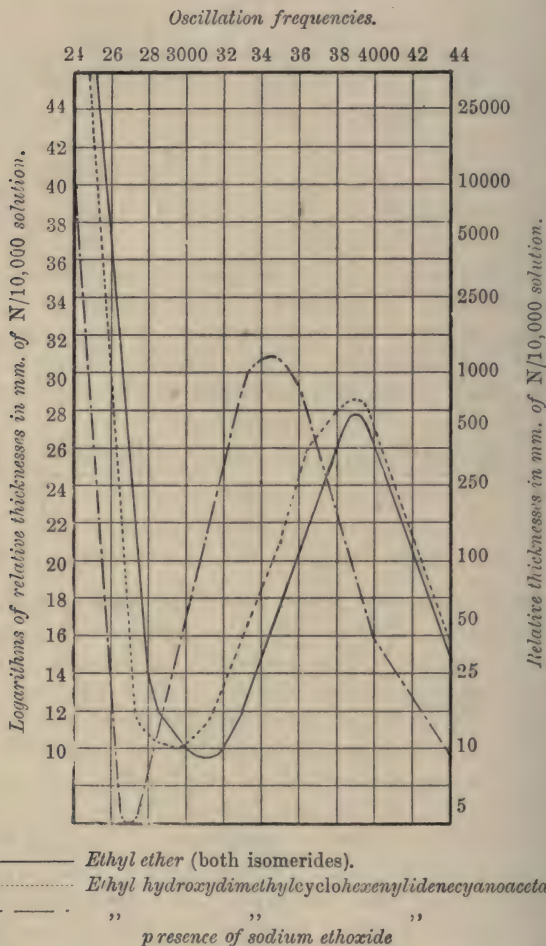
Such a formula appears to account for all the observed properties of the substance, for example, the formation of condensation products with aniline and methylaniline; its marked acidic properties, and the formation of two isomeric methyl and ethyl derivatives, which would be represented as *cis*- and *trans*-modifications:



The question naturally arises, Have the two corresponding *cis*- and *trans*-forms of ethyl hydroxydimethylcyclohexenylidenecyanoacetate been observed? The answer is in the negative. This is explained by assuming that the two forms (X) and (XI) are tautomeric, and a hydrogen atom is alternating between the two positions shown, which would preclude the possibility of fixed isomerism. The introduction of an ethyl group into the molecule causes the cessation of this mobility of the hydrogen atom, and hence fixed isomerism makes its appearance. This idea corresponds with that advanced by J. F. Thorpe (*Trans.*, 1905, **87**, 1669) to account for the fact that glutaconic acid cannot be isolated in *cis*- and *trans*-modifications, whereas its dialkyl derivatives, in which the double bond becomes fixed, are capable of existing in the two forms.

We take this opportunity of expressing our cordial thanks to Mr. E. C. C. Baly and Dr. Tuck, who have examined ethyl hydroxydimethylcyclohexenylidenecyanoacetate and its two isomeric ethyl ethers spectroscopically, and who have been kind enough to make the annexed diagram and report.

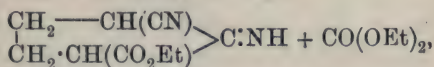
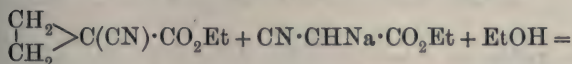
"The absorption spectra of ethyl hydroxydimethylcyclohexenylidenecyanoacetate and its two ethyl ethers were examined in alcoholic solution, and, as can be seen from the diagram, they show very persistent bands. The absorption of the two isomeric ethyl ethers is identical, and exhibits a band with its head at



$1/\lambda=3100$. The parent substance shows a band with its head at $1/\lambda=2950$, whilst in the presence of sodium ethoxide the band is shifted to $1/\lambda=2700$. This shift towards the red, on the addition of alkali, is analogous to the case of dimethyldihydroresorcin, which therefore affords evidence that labile tautomerism occurs. Since the absorption band of the parent substance is nearer to the red

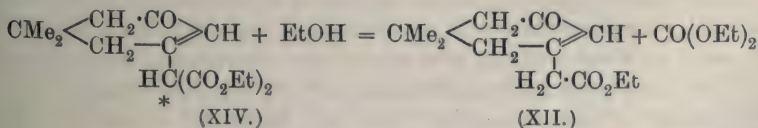
than in the case of the two ethyl ethers, the conclusion may at once be drawn that the hydrogen atom of the former is labile, which explains why the parent substance cannot be resolved into *cis*- and *trans*-modifications. That the shift in the absorption, on the addition of alkali to the parent substance, is due to the presence of labile tautomerism is proved by the fact that no change is produced by the addition of alkali to either of the ethyl ethers."

The following considerations also support the conclusion that the substance is ethyl hydroxydimethylcyclohexenylidenecyanoacetate. As already mentioned, when chlorodimethylcyclohexenone is condensed with ethyl malonate (or substituted ethyl malonates), one of the carbethoxyl groups is always eliminated as ethyl carbonate (see p. 518). Several instances of the production of the latter substance in condensation reactions have been recorded, one of the most recent being in the interaction of ethyl sodiocyanoacetate and ethyl 1-cyanocyclopropane-1-carboxylate:



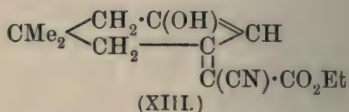
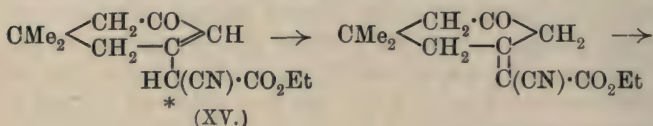
and Best and Thorpe (Trans., 1909, 95, 693) consider that the elimination of ethyl carbonate is determined, in all such cases, by spatial considerations. The present experiments lend considerable support to this view, for, in the first place, the yields of condensation products formed from chlorodimethylcyclohexenone and the substituted ethyl malonates diminished rapidly with increasing molecular weight, from which it would appear that the overcrowding in the molecule, caused by the introduction of heavier alkyl groups, renders the formation of the condensation products more and more difficult.

This affords a possible explanation of the reason for the non-acidity of ethyl dimethylcyclohexenoneacetate (XII) and the acidity of ethyl hydroxydimethylcyclohexenylidenecyanoacetate (XIII), for in the initial product of interaction (XIV) of ethyl malonate and chlorodimethylcyclohexenone, the carbon atom marked * may be regarded as overweighted and the molecule overcrowded in the region occupied by these groups, with the result that ethyl carbonate is eliminated:



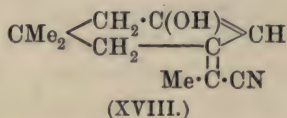
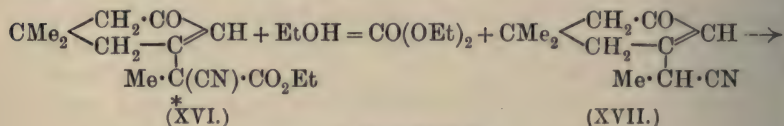
Why, then, does not a similar elimination of ethyl carbonate

take place from the condensation product (XV) formed from ethyl cyanoacetate and chlorodimethylcyclohexenone?



In this case the carbon atom marked * is not so weighted as in the substance with formula (XIV), the CN group being much lighter than a CO₂Et group, and hence the wandering of the hydrogen atom attached to this carbon atom into the ring, with formation of ethyl hydroxydimethylcyclohexenylidenecyanoacetate (XIII), sufficiently reduces the overcrowding to give a stable substance.

If, however, this hydrogen atom be replaced by a methyl group, as in the condensation of ethyl methylcyanoacetate and chlorodimethylcyclohexenone, then the carbon atom * (XVI) is again over-weighted, and as a result ethyl carbonate is eliminated:

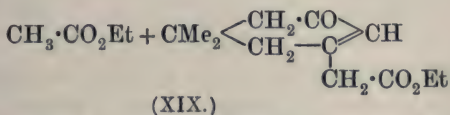
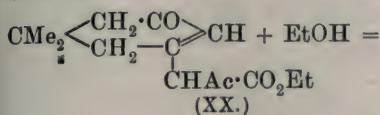


But the product so formed (XVII) is still overcrowded, and a hydrogen atom wanders into the ring, giving *hydroxydimethylcyclohexenylidenepropionitrile* (XVIII).

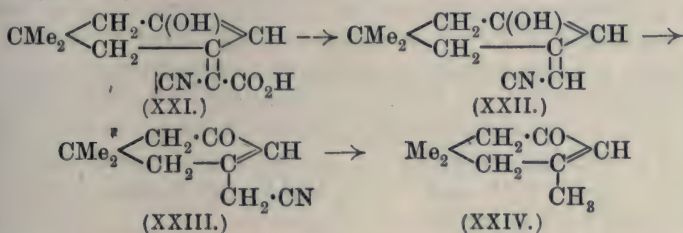
In view of these results, it seemed of interest to examine the interaction of ethyl acetoacetate and chlorodimethylcyclohexenone, when it was found that the product is the same as when using ethyl malonate, that is, ethyl dimethylcyclohexenoneacetate (XIX). Here also the initial condensation product (XX) contains the overcrowded carbon atom, marked with a *, and as a consequence the acetyl group attached to it is eliminated, by interaction with ethyl alcohol, as ethyl acetate, and a hydrogen atom takes its place.

The action of acid hydrolysing agents on ethyl hydroxydimethylcyclohexenylidenecyanoacetate can now be easily explained. The CO₂Et group (or the CN group) is first converted into CO₂H

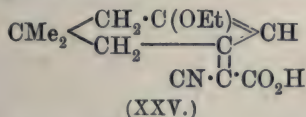
(XXI), and at once carbon dioxide is evolved, giving a substance



(XXII) which rearranges itself to dimethylcyclohexenoneacetonitrile (XXIII):



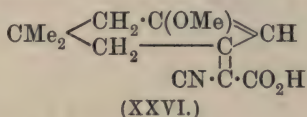
The CN group in the latter compound is then hydrolysed to $\text{CO}_2 \text{H}$, carbon dioxide is eliminated, and trimethylcyclohexenone (XXIV) produced. The acid hydrolysis of the methyl or ethyl ethers of ethyl hydroxydimethylcyclohexenylidenecyanoacetate takes place in a similar way, but the action of alkaline hydrolysing agents on these substances is of quite a different nature. When either of the two ethyl ethers is heated with an ethyl-alcoholic solution of potassium hydroxide, the carbethoxy-group is attacked, yielding *ethoxydimethylcyclohexenylidenecyanoacetic acid* (XXV), melting at 149° , which acid should exist in *cis*- and *trans*-forms, correspond-



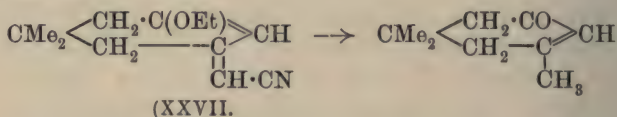
ing with the two ethyl esters. These modifications have not, however, been isolated, as no matter which of the two esters is hydrolysed, one and the same product is obtained; and it can only be concluded that, under the influence of the hydrolytic agent, the less stable form of the acid is converted into the more stable form, such cases being common among hydroaromatic substances.

When either of the methyl esters of ethyl hydroxydimethylcyclohexenylidenecyanoacetate is hydrolysed with methyl-alcoholic potassium hydroxide, *methoxydimethylcyclohexenylidenecyanoacetic acid* (XXVI), melting at 174° , is produced; but when the hydrolysis of the methyl ethers is carried out in ethyl-alcoholic

solution, ethoxydimethylcyclohexenylidenecyanoacetic acid (XXV), melting at 149°, is formed. The ease with which the methyl group



is replaced by ethyl is quite remarkable. An exactly similar phenomenon is observed when either form of ethoxydimethylcyclohexenylidenecyanoacetate is hydrolysed with methyl-alcoholic potassium hydroxide, the ethyl group being replaced by methyl, with production of methoxydimethylcyclohexenylidenecyanoacetic acid, melting at 174°. Such replacements of ethyl by methyl and vice versa in esters have been frequently recorded (compare Purdie, *Trans.*, 1885, **47**, 855; 1887, **51**, 627; 1888, **53**, 391; 1891, **59**, 468). When ethoxydimethylcyclohexenylidenecyanoacetic acid is heated a few degrees above its melting point, carbon dioxide is evolved, and 3-ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-acetonitrile (XXVII) is formed:



Although somewhat stable towards alkalis (see page 532), this nitrile is readily hydrolysed by acids, with formation of trimethylcyclohexenone.

EXPERIMENTAL.

Forty-eight grams (1 mol.) of chlorodimethylcyclohexenone were gradually added to a mixture of 70 grams (2 mols.) of ethyl cyanoacetate and 13.8 grams (2 atoms) of sodium dissolved in 170 c.c. of absolute alcohol, when a vigorous reaction at once commenced, and the liquid turned red. After heating in a water-bath for six hours, the product was poured into water and extracted four times with ether.* The aqueous alkaline liquid was then acidified with sulphuric acid, extracted four times with ether, and the ethereal solution washed, dried, and evaporated. The solid residue, weighing 51 grams after drying on porous plate, was purified by crystallisation, first from benzene, then from aqueous methyl alcohol, and analysed:

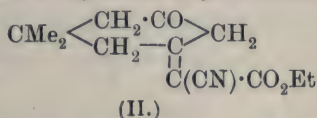
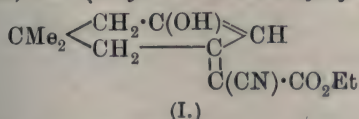
* On evaporating the ether, a residue was obtained, which was proved to consist principally of unchanged ethyl cyanoacetate and a resinous product, which yielded a solid, crystallising from methyl alcohol in fine white needles, melting at 57°, but in too small an amount for complete investigation.

0.1081 gave 0.2637 CO_2 and 0.0745 H_2O . $\text{C}=66.53$; $\text{H}=7.66$.

0.2905 „, 13.8 c.c. N_2 (moist) at 13° and 762 mm. $\text{N}=5.63$.

$\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$ requires $\text{C}=66.38$; $\text{H}=7.23$; $\text{N}=5.95$ per cent.

Ethyl 3-hydroxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetate, I (*ethyl 1:1-dimethylcyclohexan-3-onylidene-5-cyanoacetate*,



II), is easily soluble in the cold in acetone, chloroform, alcohol, or ethyl acetate, and crystallises from benzene or aqueous methyl alcohol in fine white, glistening needles, melting at 141° . It gives with ferric chloride in alcoholic solution a fine emerald-green colour, slowly fading to olive-green, a process which is hastened by warming, and with ferric chloride in neutral solution it forms a dark green precipitate. It has a marked acid reaction in aqueous solution, and can be titrated with potassium hydroxide solution, when it behaves as a monobasic acid:

0.2412 required 10.4 c.c. $\text{N}/10\text{-KOH}$. Calculated, 10.3 c.c.

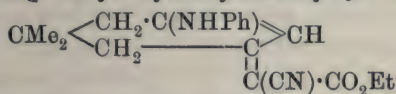
Found, M.W.=232. $\text{C}_{13}\text{H}_{17}\text{O}_3\text{N}$ requires M.W.=235.

The *silver* salt, prepared in the usual manner, is a yellow, amorphous precipitate, which darkens rapidly on exposure to air and light:

0.2618 gave 0.0828 Ag. $\text{Ag}=31.62$.

$\text{C}_{13}\text{H}_{16}\text{O}_3\text{NAg}$ requires $\text{Ag}=31.58$ per cent.

Ethyl 3-anilino-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-acetate, prepared by heating ethyl hydroxydimethylcyclohexenylidenecyano-

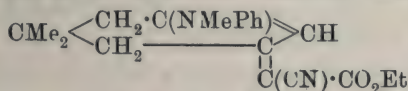


acetate with aniline, is readily soluble in acetone, alcohol, or acetic acid, insoluble or only slightly soluble in light petroleum, benzene, or chloroform, and crystallises from methyl alcohol in felted masses of long, feathery, golden-yellow needles, melting at 197° :

0.2006 gave 14.6 c.c. N_2 (moist) at 6° and 752 mm. $\text{N}=8.77$.

$\text{C}_{19}\text{H}_{22}\text{O}_2\text{N}_2$ requires $\text{N}=9.03$ per cent.

Ethyl 3-methylanilino-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetate was prepared in a similar manner, using methylaniline



instead of aniline. It separates from methyl alcohol in small, transparent, flattened, yellow crystals, melting at 183° :

after repeated crystallisation, separates in thin, white flakes, melting at 90° :

0.1486 gave 0.2696 CO_2 and 0.1022 H_2O . $\text{C} = 67.83$; $\text{H} = 7.64$.

$\text{C}_{14}\text{H}_{19}\text{O}_3\text{N}$ requires $\text{C} = 67.47$; $\text{H} = 7.63$ per cent.

2. With Ethyl Alcohol and Sulphuric Acid.

Ten grams of the hydroxy-compound were esterified exactly as described above, using ethyl instead of methyl alcohol, when 12.5 grams of a mixture of two esters were obtained, which were separated by fractional crystallisation from methyl alcohol into two substances, A and B, melting respectively at 106° and 97° . The relative proportions produced are much the same as in the case of the methyl esters, the isomeric form A predominating in amount.

Ethyl ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetate (A) crystallises from methyl alcohol in small, white needles, or from light petroleum (b. p. $60\text{--}80^\circ$) in clusters of beautiful elongated, prismatic needles, melting at 106° :

0.1280 gave 0.3215 CO_2 and 0.0958 H_2O . $\text{C} = 68.50$; $\text{H} = 8.31$.

0.3218 „ 15.2 c.c. N_2 (moist) at 10° and 744 mm. $\text{N} = 5.53$.

$\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C} = 68.44$; $\text{H} = 7.98$; $\text{N} = 5.32$ per cent.

The molecular weight was determined by the cryoscopic method, using benzene as solvent:

Found, M.W. = 235. $\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires M.W. = 263.

This ester has also been prepared by the action of ethyl iodide on the sodium salt of ethyl hydroxydimethylcyclohexenylidenecyanoacetate in alcoholic and in benzene solution; but the amount of pure material produced was very small, resinous products being formed, and under the conditions employed it was not found possible to isolate any of the isomeric ester melting at 97° .

The isomeric ester B, obtained from the mother liquors of A, crystallises from methyl alcohol in lustrous, transparent prisms, melting at 97° :

0.1035 gave 0.2606 CO_2 and 0.0758 H_2O . $\text{C} = 68.66$; $\text{H} = 8.14$.

$\text{C}_{15}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C} = 68.44$; $\text{H} = 7.98$ per cent.

The molecular weight, determined by the same method as used in the case of the isomeric ester, was found to be 236.

Although the observed values for the molecular weights of the two esters do not show as close an agreement with the theoretical value as might be desired, they are nevertheless of the same order, and serve to prove that the isomerism of these two substances is not due to the formation of complex molecules, but is in all probability a case of *cis-trans*-isomerism.

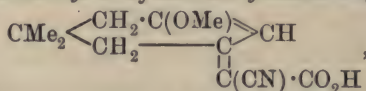
Hydrolysis of Ethyl Methoxydimethylcyclohexenylidenecyanoacetate.

Experiment showed that the same substance (m. p. 174°) was the sole product obtained when either of the esters, melting respectively at 79° and 90° , was hydrolysed with methyl-alcoholic potassium hydroxide, and therefore, for the purpose of investigating the nature of the substance melting at 174° , there was no object in first separating the two esters by the tedious process of fractional crystallisation. Four grams of the mixture of the two isomeric esters were therefore heated for two hours on the water-bath with 3 grams of potassium hydroxide dissolved in 60 c.c. of absolute methyl alcohol, when the solution was diluted with water and extracted once with ether, to remove any traces of unaltered ester. The aqueous solution was next acidified with sulphuric acid, extracted three times with ether, and the ethereal solution washed, dried, and evaporated. There resulted 3 grams of a solid, which was purified by crystallisation from dilute methyl alcohol, and analysed:

0.1380 gave 0.3318 CO_2 and 0.0841 H_2O . $\text{C} = 65.57$; $\text{H} = 6.77$.

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{C} = 65.16$; $\text{H} = 6.78$ per cent.

3-Methoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid,



crystallises from dilute methyl alcohol in masses of irregular plates, melting at 174° . At 179° a steady evolution of carbon dioxide occurs, with production of methoxydimethylcyclohexenylideneacetonitrile (compare the hydrolysis of the corresponding ethoxy-derivative, p. 531).

The presence of a methoxyl group in this acid was confirmed by a Zeisel determination:

0.2353 gave 0.2424 AgI . $\text{OMe} = 13.6$.

$\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$ requires $\text{OMe} = 14.00$ per cent.

It is interesting to note that when the hydrolysis of ethyl methoxydimethylcyclohexenylidenecyanoacetate is carried out in ethyl-alcoholic solution, the methyl of the methoxyl group is replaced by an ethyl group, the product being ethoxydimethylcyclohexenylideneacetic acid, melting at 149° (compare p. 531).

Hydrolysis of Ethyl Ethoxydimethylcyclohexenylidenecyanoacetate.

The following experiments were carried out both with the ester A, melting at 106° , and with the ester B, melting at 97° , and as

the products of hydrolysis are the same, no matter which of the two isomerides is employed, the description of the experiments applies to either of them.

1. *With Hydrochloric Acid*.—Eight and a-half grams of the ester were heated with 100 c.c. of concentrated hydrochloric acid under a reversed condenser for five hours, when, after extracting with ether and working up in the usual way, 5 grams of an oil were obtained, boiling at 104—107°/25 mm. This fraction was identified as trimethylcyclohexenone by preparing from it the semicarbazone, which melted at 193°, and the oxime, which melted at 77—78°.

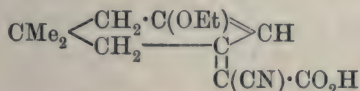
2. *With Potassium Hydroxide*.—Twenty-four grams of the ester were heated for two hours on the water-bath with 15 grams of potassium hydroxide dissolved in 200 c.c. of ethyl alcohol (if methyl alcohol is employed instead of ethyl alcohol, methoxydimethylcyclohexenylidenecyanoacetic acid is the product), and the product worked up as described in the case of ethyl methoxydimethylcyclohexenylidenecyanoacetate (see page 530), when a solid was obtained, which was crystallised from aqueous alcohol and analysed:

0.1114 gave 0.2718 CO₂ and 0.0731 H₂O. C=66.54; H=7.29.

0.2009 „ 9.4 c.c. N₂ (moist) at 8° and 752 mm. N=5.59.

C₁₃H₁₇O₃N requires C=66.38; H=7.23; N=5.95 per cent.

3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-cyanoacetic acid is readily soluble in all the ordinary organic solvents, except light



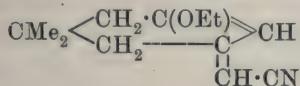
petroleum. It crystallises from aqueous methyl or ethyl alcohol in clusters of minute needles, which melt and decompose at 149°, gas being steadily evolved at 153°.

The molecular weight was determined by titration against standard potassium hydroxide solution, using phenolphthalein as indicator:

0.1901 required 7.92 c.c. N/10-KOH. Calculated, 8.09 c.c.

Found, M.W.=240. C₁₃H₁₇O₃N requires M.W.=235.

3-Ethoxy-1:1-dimethyl- Δ^3 -cyclohexenylidene-5-acetonitrile was prepared by heating 5 grams of ethoxydimethylcyclohexenylidene-



cyanoacetic acid under diminished pressure. A little above the melting point of the acid, carbon dioxide was given off, and as

soon as the evolution had ceased, the residual liquid was distilled, when the whole (3.7 grams) boiled at 162—164°/18 mm.:

0.2272 gave 13.2 c.c. N_2 (moist) at 8° and 768 mm. $N=7.10$.

$C_{12}H_{17}ON$ requires $N=7.32$ per cent.

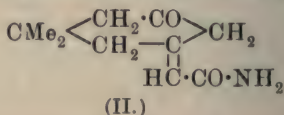
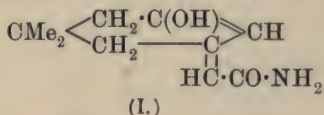
The pure substance is a colourless, highly refractive, oily liquid, boiling at 163°/18 mm., and possessing an odour of hydrocyanic acid. A Zeisel determination, carried out according to Perkin's modified method, gave the following result:

0.2468 gave 0.2745 AgI. $OEt=21.3$.

$C_{12}H_{17}ON$ requires $OEt=23.5$ per cent.

This result is somewhat low, but various investigators have found that ethoxyl determinations generally come out from 1 to 2 per cent. below the calculated figure.

The nitrile is only very slowly attacked by potassium hydroxide in alcoholic solution, giving a small amount of a substance crystallising from a mixture of chloroform and light petroleum, melting at 130°, and giving, on analysis, numbers agreeing with a formula $C_{10}H_{15}O_2N$. It is probably, therefore, hydroxydimethylcyclohexenylideneacetamide (I), or, as it is devoid of any acid nature, it may be this substance in the isomeric ketonic form (II).



When heated with concentrated hydrochloric acid, 8.5 grams of the nitrile gave 5 grams of a liquid having a camphoraceous odour, and boiling constantly at 105°/25 mm. This substance was identified as trimethylcyclohexenone by preparing the oxime, which melted at 78°, nor was this melting point lowered by admixture with an equal quantity of the oxime of pure trimethylcyclohexenone.

Action of Ethyl Methylcyanoacetate on Chlorodimethylcyclohexenone.

Ethyl methylcyanoacetate was prepared by the interaction of ethyl sodiocyanoacetate and methyl iodide, according to the directions of Auwers (*Annalen*, 1895, **285**, 283). The product, although stated by Auwers to be pure ($N=10.93$; calculated, 11.02 per cent.), boiled for the most part at 190—195°, and subsequent experiments showed that it undoubtedly contained considerable amounts of ethyl cyanoacetate and also ethyl dimethylcyanoacetate, which substances, if present in equivalent amounts, would account for the correct value for nitrogen quoted by Auwers.

Twenty-four grams of chlorodimethylcyclohexenone were added to a mixture of 39 grams (2 mols.) of ethyl methylcyanoacetate and 7 grams of sodium (2 atoms) dissolved in 42 c.c. of absolute ethyl alcohol. After heating on a water-bath for six hours, the reaction mixture was poured into water, extracted four times with ether (aqueous solution=A), the ethereal solution washed, dried, evaporated, and the residual liquid distilled in a current of steam, when all but a negligible quantity of a sticky resin passed over.

The distillate, after extraction with ether, etc., yielded 24 grams of a liquid, which, after repeated fractionation, gave two main portions of about equal weight, boiling at 126—127° and 190—195°, the latter consisting of ethyl methylcyanoacetate.

The *fraction* 126—127°, from its odour and boiling point, appeared to be ethyl carbonate, and its identity with that substance was established by analysis:

0.1406 gave 0.2629 CO_2 and 0.1068 H_2O . $\text{C}=50.99$; $\text{H}=8.44$.

$\text{C}_5\text{H}_{10}\text{O}_3$ requires $\text{C}=50.85$; $\text{H}=8.47$ per cent.

The above-mentioned aqueous alkaline solution A was acidified with sulphuric acid, extracted with ether, and, after working up in the usual manner, yielded 32 grams of a viscid, oily liquid, which, after some time, partly solidified. The solid (5 grams) was separated by spreading on porous plate, and, after crystallisation from benzene, melted at 141°, nor was this melting point altered on mixing with ethyl hydroxydimethylcyclohexenylidenecyanoacetate (see p. 528). The formation of this ester is undoubtedly due to the unchanged ethyl cyanoacetate contained in the ethyl methylcyanoacetate employed.

The oil, recovered from the porous plate by extraction with ether, did not further solidify, and could not be distilled, even under diminished pressure, without decomposing. It was therefore esterified by boiling for four hours with 300 c.c. of ethyl alcohol containing 5 per cent. of sulphuric acid. The resulting solution was worked up as already described, and the residue (18 grams) distilled under 32 mm. pressure, when the following fractions were collected:

100—150° = 3.7 grams;	150—170° = 0.4 gram;
170—195° = 6.5 grams;	195—220° = 2.4 grams.

The *fraction* 100—150° consisted principally of ethyl dimethylmalonate, for on hydrolysis it yielded dimethylmalonic acid, melting at 193° with evolution of gas:

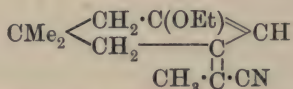
0.1088 gave 0.1824 CO_2 and 0.0597 H_2O . $\text{C}=45.72$; $\text{H}=6.10$.

$\text{C}_5\text{H}_8\text{O}_4$ requires $\text{C}=45.45$; $\text{H}=6.06$ per cent.

The presence of ethyl dimethylmalonate proves that the original

ethyl methylecyanoacetate must have contained some ethyl dimethylcyanoacetate.

The fraction 170—195°, on redistillation, passed over as a pale yellow, refractive, oily liquid, and although it did not boil very constantly (170—180°/27 mm.), analysis and subsequent hydrolysis proved it to consist of 3-ethoxy-1:1-dimethyl-Δ³-cyclohexenyldenepropionitrile:

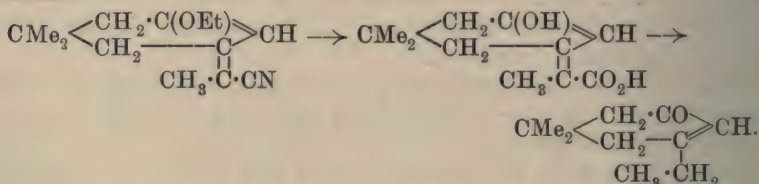


0.1145 gave 0.3178 CO₂ and 0.0951 H₂O. C=75.70; H=9.23.

C₁₀H₁₉ON requires C=76.09; H=9.26 per cent.

The mechanism of the reaction giving rise to the corresponding hydroxydimethylcyclohexenyldenepropionitrile has been already explained (see p. 524).

Seven grams of the above nitrile were heated with 100 c.c. of concentrated hydrochloric acid for five hours under a reversed condenser. The product was poured into water, extracted four times with ether, the ethereal solution washed first with sodium hydroxide solution, then with water, dried, evaporated, and the residue (5 grams) distilled, when it boiled constantly at 119.5°/25 mm. as a colourless, refractive liquid, which proved to be dimethylethylcyclohexenone (compare Trans., 1909, **95**, 28), the formation of which substance takes place in accordance with the following scheme:



0.1371 gave 0.3952 CO₂ and 0.1312 H₂O. C=78.61; H=10.63.

C₁₀H₁₆O requires C=78.94; H=10.53 per cent.

The oxime, prepared in the usual manner, is a viscid, oily liquid, boiling at 153°/28 mm., and solidifying on cooling to radiating clusters of flattened, transparent needles, melting at 43—45°. It is so readily soluble in all the ordinary organic solvents that it was found to be most easily purified by distillation:

0.1921 gave 14 c.c. N₂ (moist) at 18° and 763 mm. N=8.45.

C₁₀H₁₇ON requires N=8.38 per cent.

As this oxime has not been previously described, a specimen was made for the purpose of comparison from pure dimethylethylcyclohexenone, obtained in the manner formerly described (*loc. cit.*).

It was found to possess properties identical with the above-mentioned oxime.

The fraction 195—230° solidified after some time. After one crystallisation from benzene, it melted at 106°, and proved to be ethyl ethoxydimethylcyclohexenylidenecyanoacetate (see page 529). It was mentioned on page 533 that when the aqueous alkaline liquid A was acidified with sulphuric acid, 5 grams of ethyl hydroxydimethylcyclohexenylidenecyanoacetate separated, but evidently this separation is not a complete one, and the unaltered material is converted into its ethyl ether (m. p. 106°) during the process of esterification to which the residue was submitted.

Action of Ethyl Acetoacetate on Chlorodimethylcyclohexenone.

Fifty-two grams (2 mols.) of freshly distilled ethyl acetoacetate were mixed with a solution of 9.2 grams of sodium (2 atoms) in 110 c.c. of absolute alcohol, and 32 grams (1 mol.) of chlorodimethylcyclohexenone added. The resulting red liquid was transferred to two soda-water bottles, which were securely corked, and then heated in a boiling-water bath for two hours. The reaction mixture was poured into water, extracted five times with ether, and the ethereal solution washed, dried, and fractionated, using a Young's rod-and-disk still-head. When the ether had passed over, a small quantity of a liquid boiling at 65—70° (residue=A) was obtained, which, after further purification, was proved to consist of ethyl acetate.

The residue A was distilled in a current of steam to remove unaltered ethyl acetoacetate, and the non-volatile portion extracted three times with ether, the ethereal solution dried and evaporated, and the residue distilled, when nearly the whole (18 grams) passed over at 181°/27 mm.:

0.1242 gave 0.3106 CO₂ and 0.0972 H₂O. C=68.20; H=8.69.

C₁₂H₁₈O₃ requires C=68.57; H=8.57 per cent.

These numbers indicated that the substance was ethyl 1:1-dimethyl- Δ^4 -cyclohexen-3-one-5-acetate (Trans., 1909, **95**, 23), and the identity of the two liquids was established by hydrolysing the above product with alcoholic potassium hydroxide (*loc. cit.*), when it yielded trimethylcyclohexen-3-one, boiling at 99°/18 mm., characterised by the preparation of its oxime, which melted at 77—78°.

The authors take this opportunity of expressing their thanks to the Research Fund Committee of the Chemical Society for a grant which has, in part, defrayed the expenses of this investigation.

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LVII.—*The Influence of Colloids and Fine Suspensions on the Solubility of Gases in Water. Part I. Solubility of Carbon Dioxide and Nitrous Oxide.*

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For many years the problem of the absorption of gases, more especially of oxygen and carbon dioxide, by blood has claimed the attention of physiologists. In the case of oxygen the absorption has been regarded as being due, in greatest measure, to the formation of a compound with the hæmoglobin of the blood; whereas, in the case of carbon dioxide, the increased absorption as compared with a corresponding salt solution has been attributed to the reputed alkalinity of the blood, and the consequent formation of carbonate and bicarbonate.

In recent years, however, different investigators (compare Hoeber, *Pflüger's Archiv*, 1903, **99**, 572; Farkas, *ibid.*, 1903, **98**, 551; Friedenthal, *Verworn's Archiv f. allgem. Physiologie*, 1904, **4**, 44; van Westenryk, *Arch. exp. Path. Pharm. Suppl.*, 1908, p. 517) have shown by different methods that blood-serum is practically "water-neutral." In view of these results, it seemed that possibly the absorption of carbon dioxide by the blood had been ascribed too exclusively to the alkalinity of blood, and it seemed not improbable that the colloids present in blood play an important rôle (Findlay and Harby, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 169; Wo. Ostwald, *ibid.*, 1908, **2**, 264). Before this view could be tested, it was necessary to study the influence of colloids of various kinds on the absorption of gases, since our knowledge of this depended almost entirely on the few experiments carried out by Geffchen (*Zeitsch. physikal. Chem.*, 1904, **49**, 298).

Preliminary experiments had shown that the increased absorption of carbon dioxide which occurred under atmospheric pressure in presence of certain colloids was due, probably, to chemical interaction. To obtain a deeper insight into the influence of colloids on gas solubility, it was deemed of importance to study the solubility under a series of pressures, and also to exclude effects due to chemical combination by studying the absorption of a neutral gas, nitrous oxide (with regard to the neutrality of nitrous oxide, see Geffchen, *loc. cit.*, p. 301). This gas was chosen because its solubility in water is nearly the same as that of carbon dioxide. Experiments on the lines indicated were carried out during the year 1908-9, the influence of ferric hydroxide, gelatin, arsenious sulphide, silicic acid,

dextrin, starch, glycogen, egg-albumen, and serum-albumen, as well as suspensions of charcoal and silica, on the absorption of carbon dioxide and nitrous oxide having been investigated at pressures varying from about 750 mm. to 1400 mm. of mercury.

Apparatus.

The apparatus employed was, in its essential points, the same as that used by Geffchen (*loc. cit.*), the manometer tube, however, being graduated and considerably lengthened to permit of absorptions being carried out at pressures higher than atmospheric. The burette was connected with the absorption pipette by means of capillary copper tubing, in order to impart the necessary flexibility to the apparatus. The burette was contained in a glass mantle through which water was caused to circulate, the temperature being maintained constant within 0.1° throughout a determination.

So long as the absorption of gas was allowed to take place under atmospheric pressure only, the dead space (that is, the ungraduated portion at the top of the burette and the volume of the tubes connecting it with the absorption vessel) does not require to be taken account of, as the initial and final conditions under which the gas is measured are the same. When, however, the absorption is allowed to take place at higher pressures, the volume of the dead space must be known. This was ascertained by measuring the total contraction of a known volume of gas and the volume in the dead space, produced by a known increase of pressure.

Since the gas in the measuring burette was always kept dry, the point of saturation of the solution with gas was approached from the side of least pressure only, but precautions were taken to make sure that the process of absorption at any given pressure was complete.

The liquid used for the absorption of the gas was previously well boiled to free it from air; or in those cases where boiling was not permissible, the liquid was freed from air by being placed under diminished pressure.

In all the following experiments the temperature of absorption was 25.0° , and the experimental error did not exceed ± 0.25 per cent., and was in most cases less than this.

Calculation of Results.

The solubility was calculated by means of the formula:

$$\text{Solubility} = \frac{C_l}{C_g} = \frac{\left[\left(\frac{v_1 P}{P+p} \cdot \frac{T}{T_1} - \frac{v_2 T}{T_2} \right) \left(\frac{P+p}{P+p-p'} \right) \right]}{V_2} - V_1,$$

where

C_l = concentration of the gas in the liquid phase.

C_g = " " " " gaseous phase.

v_1 = initial volume of the gas in the burette measured at the pressure P .

v_2 = final volume of the gas in the burette measured under the pressure $P + p$.

T = absolute temperature of experiment (thermostat temperature).

T_1 = absolute temperature of the gas in the burette at the beginning of the experiment when v_1 was measured.

T_2 = absolute temperature of the gas in the burette at the end of the experiment when v_2 was measured.

P = barometric pressure.

p = increase of pressure as shown by the manometer.

p' = vapour pressure of the liquid in the absorption pipette at the temperature T .

V_1 = volume of the gas space in the pipette at the temperature T .

V_2 = volume of absorbing liquid in the pipette.

The volume v_2 was corrected, when necessary, for the dead space of the apparatus. Considering the experimental errors of determination, no correction was applied to the burette readings for cubical expansion of glass, nor were the barometric readings corrected for temperature.

I.—Solubility of Carbon Dioxide.

The carbon dioxide employed for the following experiments was the commercial product, which analysis showed to contain 0.58 per cent. of impurity. The following values were found for its solubility in pure water at 25° (table I):

TABLE 1.—Solubility of Carbon Dioxide in Water.

Pressure (mm. Hg) ...	752	800	955	1059	1153	1351
Solubility	0.817	0.815	0.816	0.817	0.818	0.820
Pressure	743	841	955	1064	1243	1351
Solubility	0.816	0.817	0.817	0.819	0.819	0.820

As the mean of these and a number of other determinations we obtained the value 0.817 for the solubility of the carbon dioxide employed, the solubility being independent of the pressure within the limits of experimental error. The value found by Geffcken for pure carbon dioxide was 0.826.

(a) *Ferric Hydroxide Solution.*

In preparing the solution of ferric hydroxide, the method recommended by A. A. Noyes (*J. Amer. Chem. Soc.*, 1905, **37**, 94) was employed. To a molar solution of ferric chloride, molar ammonium carbonate solution was added until the precipitate which formed on each addition barely dissolved. This mixture was then thoroughly dialysed, first against tap water, and finally against distilled water, until soluble salts were removed. The concentration of the solution was determined by precipitation of the hydroxide with ammonium sulphate.

FIG. 1.

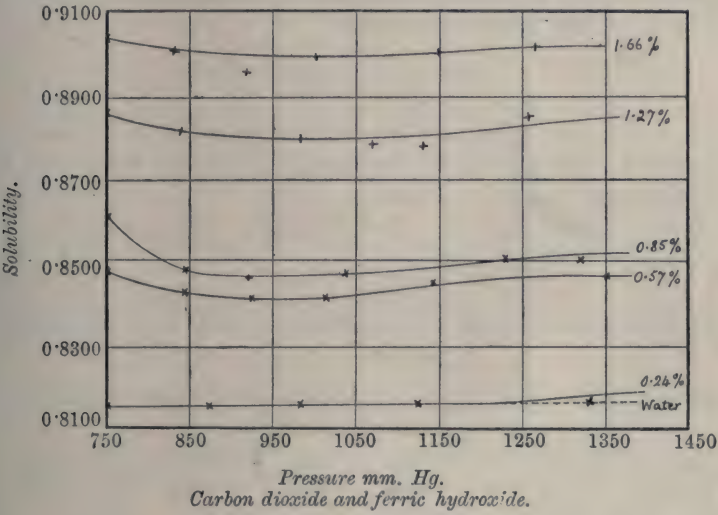


TABLE 2.—*Solubility of Carbon Dioxide in Ferric Hydroxide Solutions (see Fig. 1).*

Concentration: 0.569 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.000.

Pressure	750	846	928	1015	1146	1356
Solubility	0.848	0.843	0.841	0.842	0.845	0.846

Concentration: 0.854 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.003.

Pressure	750	847	923	1040	1234	1322
Solubility	0.862	0.858	0.856	0.857	0.860	0.861

Concentration: 1.277 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1.005.

Pressure	746	841	985	1071	1133	1256
Solubility	0.886	0.881	0.880	0.878	0.878	0.887

TABLE 2 (*continued*).Concentration: 1.661 grams of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.

Density = 1.009.

Pressure	747	831	918	1002	1150	1267
Solubility	0.904	0.901	0.896	0.900	0.900	0.902

Geffchen (*loc. cit.*) has stated that the comparatively rapid initial absorption of carbon dioxide is succeeded by a slow further absorption. In our experiments this slow absorption was barely appreciable except at higher pressures, and was, even then, not great.

The above numbers, when plotted, show that the increase of solubility under atmospheric pressure is proportional to the concentration of the ferric hydroxide.

(b) *Dextrin*.

The dextrin employed was the purest supplied by Kahlbaum. It contained a slight quantity of impurity insoluble in water, and this was separated from the solutions before they were used for absorbing carbon dioxide. The solubility values are given in table 3.

TABLE 3.—*Solubility of Carbon Dioxide in Dextrin Solutions.*

(See also Fig. 2).

Concentration: 3.50 grams of dextrin in 100 c.c. of solution.

Density = 1.008.

Pressure	753	819	888	1060	1171	1262
Solubility	0.799	0.800	0.800	0.800	0.801	0.803

Concentration: 5.60 grams in 100 c.c. of solution. Density = 1.015.

Pressure	754	806	856	971	1078	1247
Solubility	0.785	0.785	0.784	0.787	0.787	0.791

Concentration: 9.50 grams in 100 c.c. of solution. Density = 1.034.

Pressure	753	817	864	960	1115	1286
Solubility	0.761	0.756	0.758	0.759	0.764	0.768

Concentration: 13.00 grams in 100 c.c. of solution. Density = 1.040.

Pressure	741	798	882	962	1131	1256
Solubility	0.746	0.741	0.742	0.745	0.749	0.751

Concentration: 18.90 grams in 100 c.c. of solution. Density = 1.064.

Pressure	748	846	934	1031	1180	1344
Solubility	0.715	0.710	0.713	0.716	0.720	0.725

Concentration: 20.60 grams in 100 c.c. of solution. Density = 1.069.

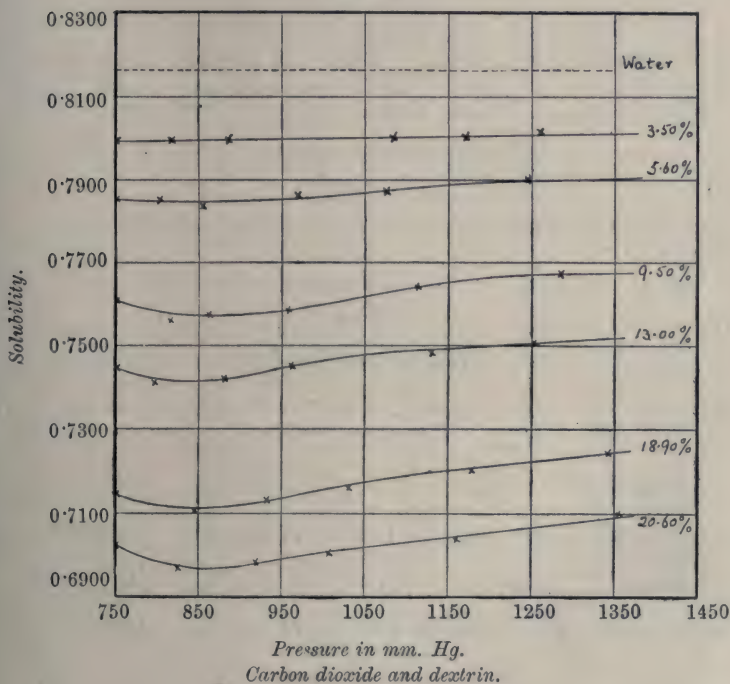
Pressure	728	826	920	1008	1161	1356
Solubility	0.703	0.697	0.698	0.700	0.704	0.710

As shown in Fig. 8, the solubility diminishes in almost exact proportionality with the increase in concentration of the dextrin.

(c) *Arsenious Sulphide.*

The arsenious sulphide was prepared by passing hydrogen sulphide into a solution of pure arsenious oxide until the latter was saturated. The greater part of the excess of hydrogen sulphide was then expelled by bubbling hydrogen through the liquid, which was then filtered before being used. As colloidal solutions of arsenious

FIG. 2.



sulphide decompose on boiling, the last traces of dissolved air were removed by placing the liquid under diminished pressure, although this led to the formation of a very thin film on the surface of the liquid. This behaviour is similar to the formation of films on the surface of peptone solutions observed by Metcalf (*Zeitsch. physikal. Chem.*, 1905, **52**, 1), and is no doubt to be regarded similarly as an illustration of Gibbs's principle of increased surface concentration.

The amount of arsenious sulphide in the solutions was determined

by precipitating with hydrochloric acid and drying the precipitate at 80°.

TABLE 4.—*Solubility of Carbon Dioxide in Solutions of Arsenious Sulphide.*

Concentration: 0.392 gram of As_2S_3 in 100 c.c. of solution.
Density = 0.997.

Pressure	756	891	951	1047	1172	1259
Solubility	0.816	0.817	0.814	0.816	0.818	0.820

Concentration: 1.410 grams in 100 c.c. of solution. Density = 1.003.

Pressure	756	851	972	1082	1137	1281
Solubility	0.810	0.810	0.812	0.810	0.812	0.811

Concentration: 2.289 grams in 100 c.c. of solution. Density = 1.007.

Pressure	754	853	938	1003	1068	1211
Solubility	0.806	0.806	0.806	0.806	0.806	0.806

(d) *Starch.*

For these experiments Kahlbaum's pure soluble starch was employed.

TABLE 5.—*Solubility of Carbon Dioxide in Solutions of Starch.*
(See also Fig. 3.)

Concentration: 2.50 grams of starch in 100 c.c. of solution.
Density = 1.009.

Pressure	752	849	951	1050	1182	1334
Solubility	0.796	0.797	0.799	0.801	0.804	0.806

Concentration: 5.00 grams in 100 c.c. of solution. Density = 1.016.

Pressure	753	840	912	1021	1198	1298
Solubility	0.778	0.780	0.781	0.784	0.789	0.790

Concentration: 7.50 grams in 100 c.c. of solution. Density = 1.023.

Pressure	752	860	1016	1078	1201	1351
Solubility	0.762	0.764	0.767	0.769	0.772	0.774

Concentration: 10.00 grams in 100 c.c. of solution. Density = 1.030.

Pressure	758	893	982	1087	1163	1337
Solubility	0.750	0.753	0.754	0.756	0.759	0.760

It was observed in the case of the above solutions that the time required to saturate the solution with gas was much greater than in most of the other cases studied. The relation between starch concentration and solubility is shown in Fig. 8.

(e) *Gelatin.*

French sheet gelatin, which was found to be free from salts, was used. Solutions containing as much as 6 per cent. of gelatin were quite mobile at 25°.

FIG. 3.

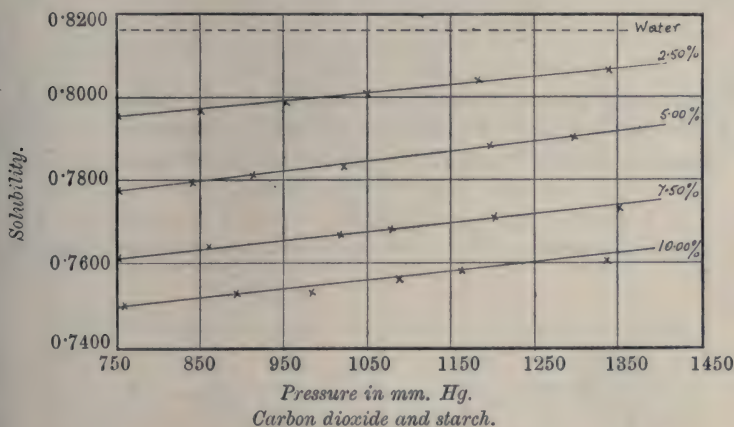


TABLE 6.—*Solubility of Carbon Dioxide in Solutions of Gelatin.*
See also Fig. 4.)

Concentration: 1.06 grams of gelatin in 100 c.c. of solution.
Density=0.999.

Pressure	746	825	901	1011	1184	1369
Solubility	0.815	0.814	0.814	0.815	0.815	0.815

Concentration: 1.68 grams in 100 c.c. of solution. Density=1.000.

Pressure	740	837	938	1072	1219	1324
Solubility	0.819	0.816	0.816	0.816	0.817	0.817

Concentration: 3.36 grams in 100 c.c. of solution. Density=1.003.

Pressure	741	826	943	1068	1220	1387
Solubility	0.826	0.819	0.818	0.818	0.819	0.820

Concentration: 6.09 grams in 100 c.c. of solution. Density=1.008.

Pressure	746	836	936	1045	1194	1371
Solubility	0.835	0.827	0.824	0.824	0.825	0.826

The influence of concentration of gelatin on the solubility at atmospheric pressure is shown in Fig. 7.

Although dilute solutions of gelatin quickly become saturated with gas, the absorption takes place more slowly in the case of the more concentrated solutions. On reducing the pressure, the gas escaped rapidly from the solution, so as to cause considerable frothing. The question of rate of evolution of gas is, however, a

special one, and, on account of its importance in various directions, will require to be investigated specially.

Further, absorption of carbon dioxide appreciably lowered the gelatinising temperature of the solution, thus producing an effect similar to peptonisation. Whether the effect is a temporary or a permanent one, we have not yet investigated.

(f) *Glycogen.*

Kahlbaum's pure glycogen was employed. In order to free it from the small quantities of the salts which it contained, it was subjected to dialysis, toluene being added to prevent putrefaction.

FIG. 4.

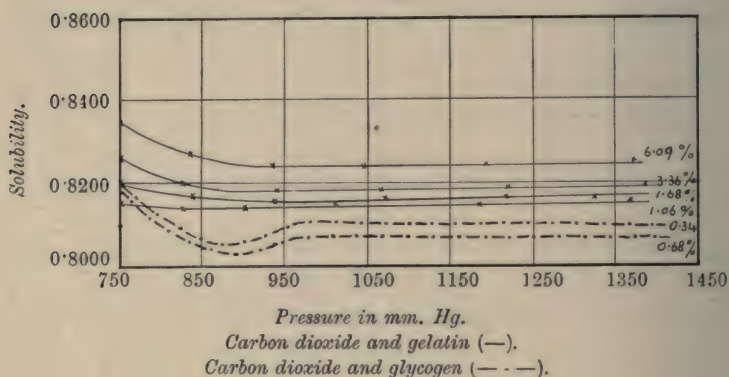


TABLE 7.—*Solubility of Carbon Dioxide in Solutions of Glycogen*
(see also Fig. 4).

Concentration: 0.34 gram of glycogen in 100 c.c. of solution.
Density=0.998.

Pressure	759	859	959	1132	1247	1369
Solubility	0.819	0.805	0.810	0.812	0.810	0.810

Concentration: 0.68 gram in 100 c.c. of solution. Density=1.000.

Pressure	759	842	954	1114	1277	1371
Solubility	0.817	0.805	0.807	0.807	0.807	0.807

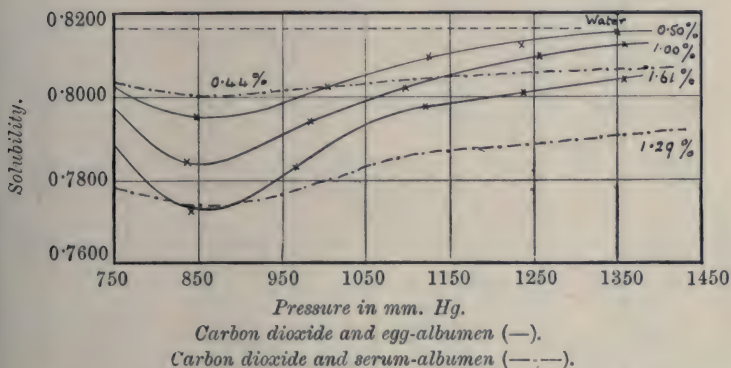
As it was impossible to remove all the toluene from the glycogen solutions, the experimental values of the solubility had to be corrected for the slight lowering of solubility produced by the toluene. The numbers in the above table are such corrected values, but they are probably not quite so accurate as in the previous cases. We may assume, however, that the relative values at different pressures and concentrations are unaffected by the correction.

(g) *Egg-Albumen.*

This was prepared from fresh eggs by the improved method of Hofmeister (*J. Physiol.*, 1898, **23**, 130). Pure crystals were obtained from the first crystalline precipitate as follows. The precipitate was washed with three changes of half saturated ammonium sulphate solution, which contained one part of glacial acetic acid per thousand. The crystals were then dissolved in the minimal quantity of water, and, while constantly stirring, a saturated solution of ammonium sulphate was added slowly until a distinct precipitate was formed; then, in addition, further 2 c.c. of the sulphate solution were added for each 1000 c.c. of albumen solution. At the end of several days crystals were obtained.

As these crystals are not pure albumen, but contain ammonium sulphate either in combination or in solution, they were dissolved

FIG. 5.



in water and dialysed until free from ammonium salts. A small quantity of toluene was added to prevent putrefaction.

The amount of albumen in solution was determined by heating the solution until the albumen was completely coagulated, the coagulum being then dried at 100° and weighed.

TABLE 8.—*Solubility of Carbon Dioxide in Solutions of Egg-Albumen* (see also Fig. 5).

Concentration: 0.50 gram of albumen in 100 c.c. of solution.
Density=0.999.

Pressure	729	849	1004	1125	1236	1350
Solubility	0.806	0.795	0.802	0.810	0.812	0.816

Concentration: 1.00 gram in 100 c.c. of solution. Density=1.002.

Pressure	734	836	984	1089	1257	1358
Solubility	0.800	0.784	0.794	0.801	0.810	0.812

TABLE 8 (*continued*).

Concentration: 1.61 grams in 100 c.c. of solution. Density = 1.005.

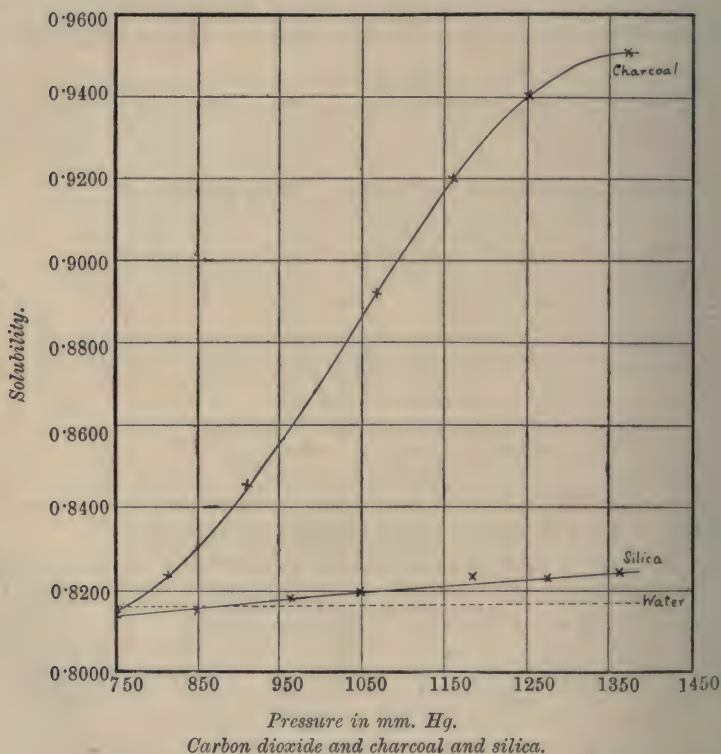
Pressure	738	841	966	1123	1239	1359
Solubility	0.791	0.773	0.783	0.797	0.801	0.804

The influence of concentration of albumen on the solubility at atmospheric pressure is shown in Fig. 7.

(h) Serum-Albumen.

Neutral serum-albumen was prepared from fresh ox-blood by a method due to Pauli. The blood-serum, to which was added a

FIG. 6.



small quantity of toluene to prevent putrefaction, was placed in small parchment cells suspended in closed glass vessels filled with distilled water. The serum was dialysed for six weeks against distilled water saturated with toluene. During the first three weeks the water was changed daily, thereafter every second day. The

concentration of the solutions was determined as in the case of solutions of egg-albumen.

TABLE 9.—*Solubility of Carbon Dioxide in Solutions of Serum-Albumen* (see also Fig. 5).

Concentration: 0.44 gram of albumen in 100 c.c. of solution.
Density = 0.998.

Pressure	748	844	945	1089	1246	1415
Solubility ..	0.804	0.800	0.802	0.804	0.806	0.806

Concentration: 1.29 grams in 100 c.c. of solution. Density = 1.000.

Pressure	744	838	966	1066	1261	1431
Solubility	0.779	0.774	0.778	0.785	0.789	0.792

The influence of concentration on the solubility at atmospheric pressure is shown in Fig. 7.

(i) *Silicic Acid.*

Solutions of silicic acid were prepared by dissolving pure silica in potassium hydroxide and adding excess of hydrochloric acid. The liquid was then dialysed, first against tap water, and then against distilled water, until free from chloride.

TABLE 10.—*Solubility of Carbon Dioxide in Solutions of Silicic Acid.*

Concentration: 1.40 grams of SiO_2 in 100 c.c. of solution.
Density = 1.000.

Pressure	731	829	936	1064	1193	1354
Solubility	0.822	0.819	0.816	0.816	0.816	0.816

Concentration: 2.20 grams in 100 c.c. of solution. Density = 1.002.

Pressure	732	836	938	1038	1178	1335
Solubility	0.828	0.822	0.820	0.820	0.820	0.820

Concentration: 2.80 grams in 100 c.c. of solution. Density = 1.003.

Pressure	731	873	960	1050	1203	1330
Solubility	0.831	0.825	0.824	0.823	0.824	0.825

In this case the solubility-pressure curves are similar in form to those for carbon dioxide and ferric hydroxide (Fig. 1).

The influence of concentration on the solubility at atmospheric pressure is shown in Fig. 7.

(j) *Suspensions of Charcoal and of Silica.*

Suspensions of Kahlbaum's well-powdered bone charcoal and of pure silica were employed. The solubility of carbon dioxide in presence of such suspensions is given in the following table:

TABLE 11 (see also Fig. 6).

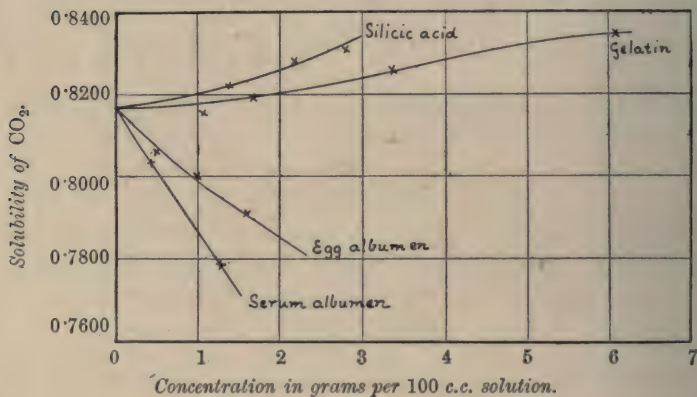
0.236 gram of charcoal in 100 c.c. Density=1.000.

Pressure	743	812	909	1069	1160	1250	1372
Solubility	0.815	0.823	0.845	0.892	0.919	0.940	0.950

0.253 gram of silica in 100 c.c. Density=1.000.

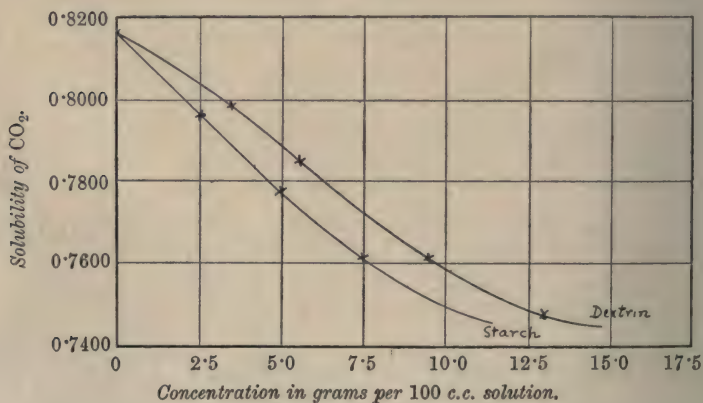
Pressure	748	849	962	1048	1182	1274	1359
Solubility	0.814	0.815	0.818	0.819	0.821	0.822	0.824

FIG. 7.



In the case of charcoal suspensions, the initial comparatively rapid absorption of gas was followed by a comparatively slow

FIG. 8.



absorption lasting from six to ten hours. The solubility values given in the above table are calculated from the maximum volume

of gas absorbed by the liquid. In the case of silica suspensions, the liquid quickly became saturated with the carbon dioxide, no slow absorption being observed.

II.—*Solubility of Nitrous Oxide.*

The nitrous oxide was prepared by heating pure ammonium nitrate in a flask at about 210—225°. Before the heat was applied, the flask was thoroughly exhausted. When the pressure of nitrous oxide in the apparatus had become equal to atmospheric pressure (a manometer was attached to the apparatus), a certain amount of the gas was allowed to escape into the air. The outlet to the air was then closed, and the nitrous oxide caused to bubble through solutions of potassium hydroxide and ferrous sulphate before being stored in a gasholder filled with brine. Before being used, it was dried by means of calcium chloride and phosphoric oxide. The solubility of the nitrous oxide in water, and in water containing colloids and suspensions, was then determined in exactly the same manner as with carbon dioxide. The following tables contain the results obtained.

TABLE 12.—*Solubility of Nitrous Oxide in Water.*

Pressure	758	842	967	1041	1185	1362
Solubility	0·592	0·593	0·592	0·593	0·592	0·592
Pressure	758	831	997	1082	1214	1351
Solubility	0·592	0·593	0·592	0·593	0·594	0·592
Pressure	758	888	971	1091	1190	1281
Solubility	0·591	0·592	0·591	0·592	0·593	0·593

From these and other similar determinations, the mean value of the solubility of nitrous oxide in water was found to be 0·592, the solubility being independent of the pressure within the limits investigated.

TABLE 13.—*Solubility of Nitrous Oxide in Ferric Hydroxide Solutions* (see also Fig. 9).

Concentration: 0·625 gram of $\text{Fe}(\text{OH})_3$ in 100 c.c. of solution.
Density = 1·001.

Pressure	758	846	934	1010	1121	1383
Solubility	0·590	0·586	0·584	0·588	0·588	0·588

Concentration: 1·49 grams in 100 c.c. of solution. Density = 1·008.

Pressure	734	828	935	1078	1215	1432
Solubility	0·586	0·579	0·577	0·581	0·585	0·586

Concentration: 4·061 grams in 100 c.c. of solution. Density = 1·029.

Pressure	754	835	883	1093	1208	1358
Solubility	0·578	0·573	0·571	0·574	0·579	0·580

Contrary to the behaviour of carbon dioxide, the solubility of nitrous oxide is lowered by ferric hydroxide, the diminution of solubility being practically proportional to the concentration, as shown in Fig. 14. Further, the behaviour of nitrous oxide is unlike that of carbon dioxide, in that there is no long period of slow absorption observable, neither at high nor at low pressures.

FIG. 9.

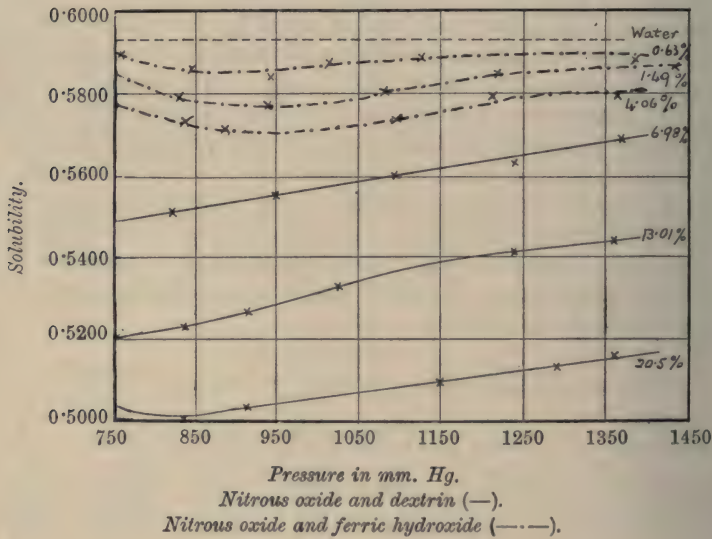


TABLE 14.—Solubility of Nitrous Oxide in Solutions of Dextrin (see also Fig. 9).

Concentration: 6.98 grams of dextrin in 100 c.c. of solution.
Density=1.018.

Pressure	739	822	949	1092	1239	1368
Solubility	0.549	0.550	0.555	0.560	0.562	0.569

Concentration: 13.01 grams in 100 c.c. of solution. Density=1.039.

Pressure	729	836	914	1023	1237	1358
Solubility	0.529	0.523	0.526	0.533	0.540	0.544

Concentration: 20.30 grams in 100 c.c. of solution. Density=1.062.

Pressure	740	836	911	1149	1290	1360
Solubility	0.503	0.499	0.503	0.509	0.513	0.516

Compare also Fig. 15.

TABLE 15.—*Solubility of Nitrous Oxide in Solutions of Arsenious Sulphide.*

Concentration: 1·85 grams of As_2S_3 in 100 c.c. of solution.
Density = 1·004.

Pressure	746	820	924	1055	1196	1346
Solubility	0·591	0·590	0·590	0·592	0·593	0·593

Concentration: 2·29 grams in 100 c.c. of solution. Density = 1·007.

Pressure	746	850	1006	1110	1209	1300
Solubility	0·590	0·586	0·588	0·589	0·589	0·590

From these figures it is seen that arsenious sulphide is without influence on the solubility of nitrous oxide.

FIG. 10.

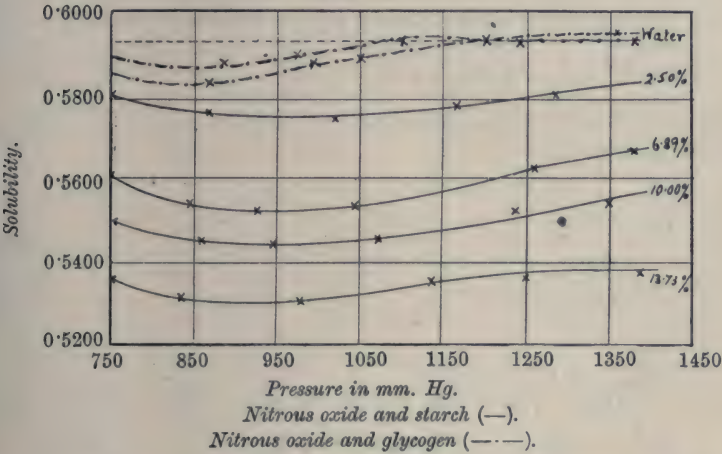


TABLE 16.—*Solubility of Nitrous Oxide in Solutions of Starch*
(see also Fig. 10).

Concentration: 2·50 grams of starch in 100 c.c. of solution.
Density = 1·009.

Pressure	742	871	1020	1166	1284	1441
Solubility	0·580	0·576	0·575	0·578	0·581	0·582

Concentration: 6·89 grams in 100 c.c. of solution. Density = 1·021.

Pressure	742	848	929	1046	1261	1381
Solubility	0·561	0·554	0·553	0·554	0·562	0·567

Concentration: 10·00 grams in 100 c.c. of solution. Density = 1·030.

Pressure	742	860	948	1071	1239	1350
Solubility	0·550	0·544	0·545	0·545	0·553	0·555

Concentration: 13·73 grams in 100 c.c. of solution. Density = 1·040.

Pressure	739	836	982	1136	1252	1387
Solubility	0·537	0·532	0·530	0·535	0·536	0·538

The influence of concentration on the solubility is shown in Fig. 15.

TABLE 17.—*Solubility of Nitrous Oxide in Solutions of Gelatin*
(see also Fig. 11).

Concentration: 1.31 grams of gelatin in 100 c.c. of solution.
Density=0.999.

Pressure	731	849	937	1069	1176	1328
Solubility	0.589	0.590	0.590	0.592	0.592	0.592

Concentration: 3.09 grams in 100 c.c. of solution. Density=1.003.

Pressure	730	858	950	1089	1230	1373
Solubility	0.581	0.582	0.584	0.586	0.588	0.588

Concentration: 6.06 grams in 100 c.c. of solution. Density=1.008.

Pressure	730	850	961	1097	1247	1379
Solubility	0.560	0.563	0.566	0.568	0.570	0.571

The influence of concentration of gelatin on the solubility is shown in Fig. 14.

FIG. 11.

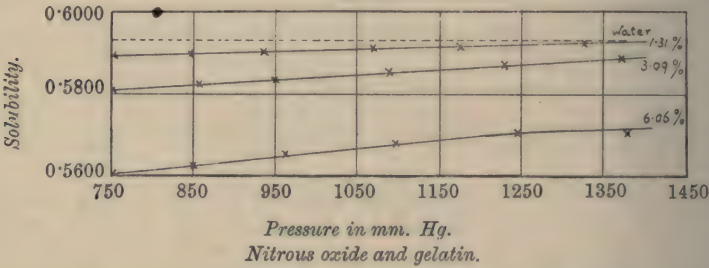


TABLE 18.—*Solubility of Nitrous Oxide in Solutions of Glycogen*
(see Fig. 10).

Concentration: 0.49 gram of glycogen in 100 c.c. of solution.
Density=0.999.

Pressure	738	889	977	1102	1239	1386
Solubility	0.590	0.588	0.591	0.594	0.594	0.594

Concentration: 1.00 gram of glycogen in 100 c.c. of solution.
Density=1.002.

Pressure	737	871	991	1050	1201	1360
Solubility	0.585	0.584	0.589	0.591	0.594	0.596

The influence of concentration of glycogen on the solubility of nitrous oxide is shown in Fig. 14.

TABLE 19.—*Solubility of Nitrous Oxide in Solutions of Egg-Albumen* (see also Fig. 12).

Concentration: 0.35 gram of albumen in 100 c.c. of solution. Density=0.998.

Pressure	735	830	954	1139	1249	1363
Solubility	0.580	0.578	0.580	0.581	0.580	0.580

Concentration: 0.75 gram in 100 c.c. of solution. Density=1.000.

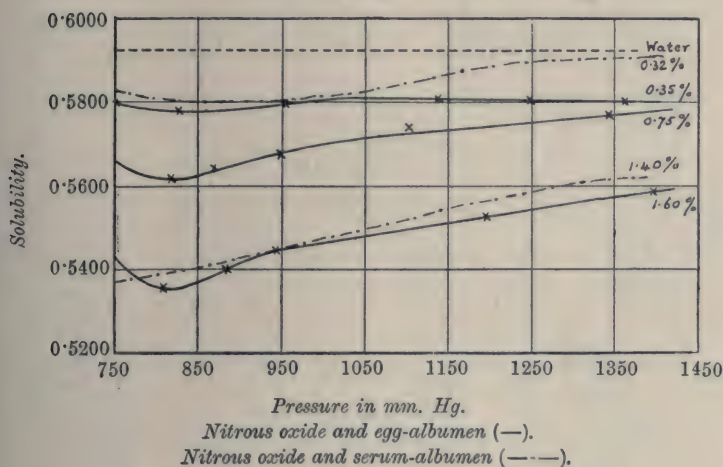
Pressure	735	820	872	951	1104	1344
Solubility	0.569	0.562	0.564	0.567	0.573	0.577

Concentration: 1.60 grams in 100 c.c. of solution. Density=1.005.

Pressure	729	811	886	946	1199	1399
Solubility	0.548	0.535	0.540	0.544	0.553	0.558

The influence of concentration on solubility is shown in Fig. 14.

FIG. 12.

TABLE 20.—*Solubility of Nitrous Oxide in Solutions of Serum-Albumen* (see also Fig. 12).

Concentration: 0.32 gram of serum-albumen in 100 c.c. Density=0.998.

Pressure	746	873	978	1126	1259	1395
Solubility	0.583	0.581	0.579	0.586	0.588	0.591

Concentration: 1.40 grams in 100 c.c. of solution. Density=1.001.

Pressure	743	842	913	1048	1228	1388
Solubility	0.537	0.538	0.545	0.550	0.558	0.562

The influence of concentration on solubility is shown in Fig. 14.

TABLE 21.—*Solubility of Nitrous Oxide in Solutions of Silicic Acid*
(see also Fig. 13).

Concentration: 1.87 grams of SiO₂ in 100 c.c. of solution.
Density=1.001.

Pressure	748	825	921	1046	1217	1349
Solubility	0.596	0.598	0.598	0.600	0.602	0.604

Concentration: 3.63 grams in 100 c.c. of solution. Density=1.005.

Pressure	741	848	994	1122	1217	1394
Solubility	0.601	0.602	0.605	0.607	0.608	0.609

The influence of concentration on the solubility is shown in Fig. 14.

FIG. 13.

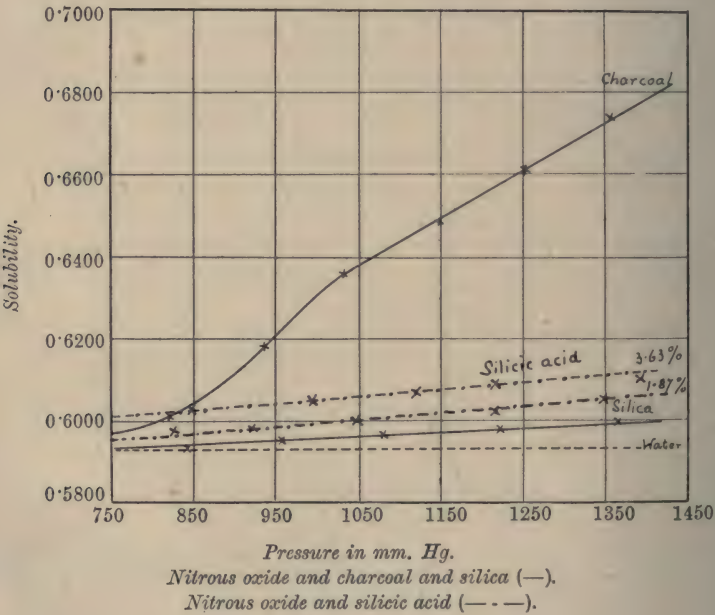


TABLE 22.—*Solubility of Nitrous Oxide in Water containing Charcoal and Silica in Suspension* (see also Fig. 13).

100 c.c. of liquid contained 0.227 gram of charcoal. Density=1.000.

Pressure	729	824	936	1034	1150	1254	1356
Solubility	0.596	0.600	0.618	0.635	0.648	0.661	0.674

100 c.c. of liquid contained 0.30 gram of SiO₂. Density=1.000.

Pressure	730	846	960	1081	1224	1365	1481
Solubility	0.592	0.593	0.595	0.597	0.597	0.600	0.602

III.—*Solubility of Carbon Dioxide in Solutions of Aniline.*

In order that the solubility curves previously obtained might be compared directly with a case where chemical combination is known to occur, the solubility of carbon dioxide in solutions of aniline was determined. The results are contained in table 23.

FIG. 14.

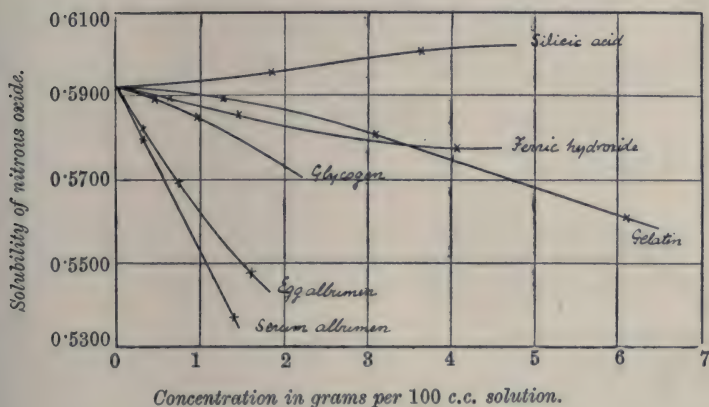


TABLE 23.

Concentration: 0.206 gram of aniline in 100 c.c. of solution.

Pressure	748	808	920	1053	1159	1243
Solubility	0.865	0.855	0.857	0.855	0.862	0.860

Concentration: 0.425 gram in 100 c.c. of solution.

Pressure	760	816	921	1150	1236	1380
Solubility	0.909	0.897	0.897	0.897	0.902	0.908

Concentration: 0.566 gram in 100 c.c. of solution.

Pressure	760	823	941	1082	1223	1341
Solubility	0.935	0.929	0.925	0.923	0.924	0.930

Concentration: 0.743 gram in 100 c.c. of solution.

Pressure	760	895	983	1063	1223	1302
Solubility	0.953	0.941	0.940	0.940	0.940	0.942

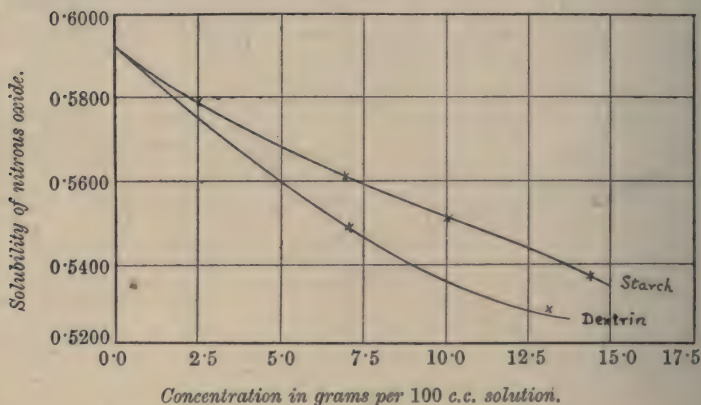
The solubility-pressure curves are similar in form to those for carbon dioxide and ferric hydroxide (Fig. 1).

IV.—*Solubility of Carbon Dioxide in Solutions of Potassium Chloride.*

Although many investigators (see Steiner, *Annalen*, 1894, **52**, 275; Gordon, *Zeitsch. physikal. Chem.*, 1895, **19**, 1; Braun, *ibid.*,

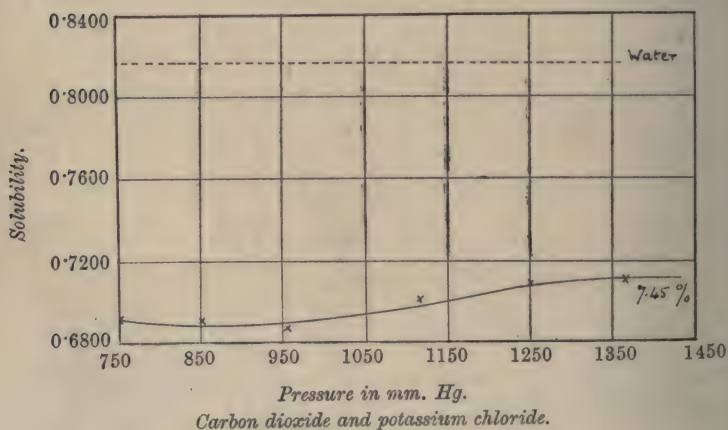
1900, 33, 721; Knopp, *ibid.*, 1904, 48, 97; Hufner, *ibid.*, 1907, 57, 611) have studied the influence of dissolved substances, both electrolytes and non-electrolytes, on the solubility of gases, such

FIG. 15.



investigations have always been made at only one pressure. In order that a comparison might be made between the influence of colloids and suspensions (emulsoids and suspensoids) and of true

FIG. 16.



solutions, the solubility of carbon dioxide in solutions of potassium chloride at different pressures was determined. The results are contained in table 24, and represented in Fig. 16.

TABLE 24 (see also Fig. 16).

Concentration: 7.45 grams of KCl in 100 c.c. of solution.

Density = 1.043.

Pressure	756	850	953	1116	1249	1362
Solubility	0.694	0.693	0.688	0.700	0.709	0.710

Concentration: 5.00 grams of KCl in 100 c.c. Density = 1.031.

Pressure	756	832	901	1050	1150	1223
Solubility	0.731	0.727	0.724	0.726	0.735	0.736

Concentration: 2.56 grams of KCl in 100 c.c. Density = 1.016.

Pressure	756	852	981	1079	1190	1362
Solubility	0.767	0.761	0.761	0.762	0.768	0.766

Discussion of Results.

A glance at the curves given on the preceding pages will show that many peculiarities of behaviour are found in the solubility of gases in liquids when that solubility is investigated, not, as previously, at only one pressure, but at different pressures. So varied, indeed, is the influence, not only in degree, but in kind, of the different solutes or pseudo-solutes and suspensions on the solubility of carbon dioxide and nitrous oxide, that conclusions drawn from the behaviour under one pressure might be very erroneous when considered for another pressure.

The substances the influence of which on the solubility of the two gases, carbon dioxide and nitrous oxide, has been studied, may be divided into emulsoids and suspensoids. To the former class belong ferric hydroxide, gelatin, starch, glycogen, egg-albumen, serum-albumen, and silicic acid; to the latter class, arsenious sulphide, charcoal, and silica. Dextrin may, perhaps, be regarded as intermediate between a true solute and an emulsoid. Aniline and potassium chloride have been included merely for the purposes of comparison.

In the case of the emulsoids, we see that *under atmospheric pressure*, silicic acid increases the solubility both of carbon dioxide and of nitrous oxide; ferric hydroxide and gelatin increase the solubility of carbon dioxide but diminish the solubility of nitrous oxide; and the other emulsoids decrease the solubility of both the gases. Of the suspensoids, arsenious sulphide is practically without influence on the solubility of either gas, while charcoal and silica increase the solubility of both gases. Lastly, dextrin decreases the solubility of both carbon dioxide and of nitrous oxide.

What the nature of the interaction may be in the case of gelatin and carbon dioxide is not, perhaps, quite easily decided.

Gelatin, as is known, is an amphoteric substance, and may therefore function as a weak base. It seems to us, however, to be doubtful if this basic property is sufficient in itself to explain the whole increase in the solubility. Possibly some more complicated action occurs, an indication of which appears to be given by the effect of carbon dioxide in lowering the gelatinisation point of gelatin solutions already referred to (p. 544). •

In the case of ferric hydroxide, as has already been pointed out by Luther and Krsnjavi (*Zeitsch. physikal. Chem.*, 1905, **46**, 170), there is probably complex ion formation. The formation of a ferric carbonate appears from the work of Raikow (*Chem. Zeit.*, 1907, **31**, 87) and of Cameron and Robinson (*J. Physical Chem.*, 1908, **12**, 561) to be excluded.

Although in these cases we may regard chemical combination as being one of the causes, perhaps the main cause, of the increased solubility of carbon dioxide, it is difficult to adopt a similar explanation in the case of silicic acid, which increases the solubility both of carbon dioxide and of nitrous oxide. In the latter case an explanation is more probably to be sought in the phenomena of adsorption (see also p. 560).

Solubility Referred to the Water in the Solutions.—With regard to the lowering effect of electrolytes and non-electrolytes on the solubility of gases in water, the view has been expressed, more especially by J. C. Philip (*Trans.*, 1907, **91**, 711), that the observed depression can be explained on the assumptions: (1) that only the water in the solution acts as solvent for the gas, and that this solvent power is not affected by the presence of the solute; (2) that the solute molecules are more or less hydrated, and therefore diminish the amount of active solvent for the gas; (3) that the gas does not dissolve in the solute, whether anhydrous or hydrated.

It must be borne in mind that the cases investigated by us are not generally comparable with those to which Philip applied his theory, for with the exceptions of the solutions of potassium chloride, and, possibly, dextrin, the solvent systems were not homogeneous, but must be regarded, most probably, as heterogeneous. And that alters the case entirely.

With regard to the solutions of potassium chloride, it may be mentioned that the values calculated for the degree of hydration vary from 6.42 to 8.68 molecules of water to one molecule of salt. These numbers are rather lower than those calculated by Philip, but not greatly so.

In the case of dextrin, however, it is evident that the solutions of dextrin show considerably different behaviour, according as the solubility of carbon dioxide or of nitrous oxide is investigated.

In the former case practically no hydration is evidenced; in the latter case a slight amount of hydration would be calculated. But in the case of carbon dioxide it will be seen that the numbers representing the solubility referred to water in the solution diminish with increase of concentration, whereas in the case of nitrous oxide, the numbers increase.

It does not appear to us that sufficient evidence has yet been adduced in support of the theory put forward by Philip. Moreover, we believe that the solubility curves which we have obtained at higher pressures show the necessity of extending the range of investigation in this direction. On this we are at present engaged.*

Change of Solubility with Pressure.—Whatever conclusions may be drawn as regards the influence of the suspensoids and emulsoids on the solubility of carbon dioxide and nitrous oxide from determinations at one pressure, they must to a greater or lesser degree be found inaccurate when applied over a range of pressures; for as the figures previously given show, the solubility is not independent of the pressure (as it is in the case of pure water), nor are the solubility curves for solutions of different concentration in all cases parallel.

Assuming that the influence of ferric hydroxide and of gelatin is mainly due to chemical combination with formation of a largely hydrolysed compound, we should expect that the solubility-pressure curve would first fall, owing to hydrolysis, and then remain nearly horizontal, owing to the diminution of hydrolysis by addition of carbonic acid. This is the type of curve obtained with aniline and ferric hydroxide, but is better seen in the case of the more weakly basic substance gelatin. Looked at in this way, the curve for carbon dioxide and silicic acid would also indicate chemical combination, and we should therefore have to assume that silicic acid is amphoteric (for which we do not know of any other evidence), or that between silicic acid and carbonic acid a reaction takes place comparable with that between silicic acid and hydrofluoric acid, the compound formed being highly hydrolysed.

As regards the influence of suspensions of charcoal and silica on the solubility of carbon dioxide and nitrous oxide, and of silicic acid on the solubility of nitrous oxide, it will be noticed that we are here dealing with curves similar to those obtained by other investigators for the absorption of gases or of dissolved substances by charcoal.

* Since this was written, a paper has appeared (this vol., p. 66) by F. L. Usher, who fails to find confirmation of the theory put forward by Philip.

Similarity is also shown by the fact that when one examines the relation between the concentration of gas in the water and in the solid, the general relationship $c_2^x/c_1 = \text{const.}$, found by previous workers for "adsorption" phenomena, also holds in the present cases. Here c_2 is the weight of gas taken up by the water in 100 c.c. of the suspension, and c_1 the weight taken up by the suspended solid. x we have found to be equal to 4.

TABLE 25.

<i>Charcoal and Carbon Dioxide, 0.236 gram of Charcoal in 100 c.c.</i>				<i>Charcoal and Nitrous Oxide, 0.227 gram of Charcoal in 100 c.c.</i>			
Pressure.	c_1 .	c_2 .	c_2^4/c_1 .	Pressure.	c_1 .	c_2 .	c_2^4/c_1 .
950	0.0086	0.1837	0.132	950	0.0059	0.1332	0.053
1000	0.0127	0.1934	0.110	1000	0.0085	0.1402	0.048
1050	0.0178	0.2030	0.099	1050	0.0109	0.1472	0.043
1150	0.0266	0.2224	0.092	1150	0.0151	0.1613	0.045
1250	0.0365	0.2417	0.098	1250	0.0200	0.1753	0.047
1350	0.0430	0.2610	0.108	1350	0.0259	0.1893	0.050

In the above cases, therefore, increased solubility would be ascribed to "adsorption," accompanied or unaccompanied by absorption.

The solubility curves so far discussed are comparatively simple in form, and the influence of the colloid or suspension may plausibly be explained on the basis of partial chemical combination or of "adsorption," accompanied or unaccompanied by absorption. In these cases the solubility of the gases is increased at all pressures.

In most of the cases examined, however, where dealing with emulsoids, the solubility of the gas is diminished even when one takes into account the volume of water in the solution. This may be explained, formally, by the assumption of hydrate formation. But even if this be accepted, the remarkable behaviour observed at higher pressures remains to be accounted for. An examination of the solubility-pressure curves shows that, with the exception of the cases already discussed, there exists for a number of the colloids a very well-defined minimum of solubility, this minimum being more marked in concentrated than in dilute solutions. In all such cases the influence of the colloid must be a very complex one, and two effects at least must enter into play, one causing a diminution of solubility with pressure, the other an increase. In dilute solutions the former is sometimes absent or negligible.

What are these two factors? So far as the rising portion of the curves is concerned, we assume that the rise is due to "adsorption," whatever the true nature of this process may be. For this portion of the different curves we have also found that the ratio $c_2^4/c_1 = \text{const.}$, as is shown by the following table:

TABLE 26.

Serum-Albumen and Nitrous Oxide.

1.40 grams of albumen per 100 c.c.

Pressure.	c_1 .	c_2 .	$\frac{c_2}{c_1}$.
915	0.0017	0.1164	0.108
1000	0.0026	0.1272	0.100
1050	0.0031	0.1336	0.103
1150	0.0047	0.1463	0.098
1250	0.0061	0.1590	0.105
1350	0.0079	0.1717	0.111

0.537 is the value of the solubility used for calculating c_2 .

A similar degree of constancy is obtained in the case of the other curves.

As regards the factor producing the lowering of the solubility, we believe that the simplest assumption to make is that of solubility of the gas in the colloid phase. As has already been pointed out, we are dealing here with heterogeneous systems, comparable with a mixture of two partly miscible liquids. So far as we are aware, the solubility of a gas in such a system has not yet been investigated; but we may very properly assume that the gas dissolves (unequally) in the two phases, namely, in the cases under discussion, in the aqueous phase and the colloid phase. We must also further assume that the solubility in the colloid phase no longer follows Henry's law, but that the solubility increases less rapidly than the pressure. Under such conditions the solubility curve would no longer be a straight line, but would fall with increase of pressure. Such a deviation from Henry's law signifies that the molecular weight of the gas in the gaseous phase and in the colloid phase is no longer the same; and we must therefore assume that the gases have a higher molecular weight in the colloid phase than in the water phase. That is, we must assume polymerisation of the gas in the colloid phase. By these assumptions we are enabled to explain, formally at least, the behaviour observed, and it must be left to future investigation to show whether the explanation is only formal or may be regarded as essential. It is clear, however, from the foregoing investigation that colloids in solution will not necessarily increase the solubility of a gas. The action is a specific one, and depends both on the colloid and on the gas.

CHEMICAL DEPARTMENT.

UNIVERSITY OF BIRMINGHAM.

LVIII.—*Absorption Spectra and Melting-point Curves of Aromatic Diazoamines.*

By CLARENCE SMITH and CONSTANCE HAMILTON WATTS.

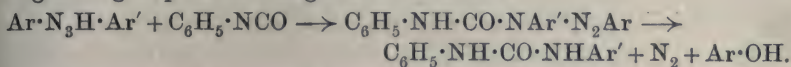
THE discovery by Griess that the same diazoamine is formed by diazotising either of two primary aromatic amines and coupling the product with the other, led twenty or thirty years ago to numerous investigations which had for their object the determination of the constitution of such mixed diazoamines and the isolation of the two possible isomeric forms, $\text{ArN}_2\cdot\text{NHAr}'$ and $\text{ArNH}\cdot\text{N}_2\text{Ar}'$. The latter purpose has never been satisfactorily realised, whilst the former has resulted in a mass of such conflicting evidence that even at the present time the constitution of the aromatic diazoamines remains an open question.

In order to show that the conclusions at which we have arrived are supported by the bulk of this earlier evidence, it is necessary to recapitulate the main points made by previous investigators, the more so as an impartial survey of all the facts appears to have been omitted hitherto.

An examination of the substances obtained by decomposing with water the product of the action of carbonyl chloride on a benzene solution of a diazoamine led Sarauw to the conclusion that the imino-group is attached to the more negative aromatic nucleus, and that the initial product (not isolated) of the reaction is a diazo-carbamide, $\text{ArN}_2\cdot\text{NAr}'\cdot\text{CO}\cdot\text{NAr}'\cdot\text{N}_2\text{Ar}$, in which Ar is the less negative benzenoid group. A perusal of the author's two papers (*Ber.*, 1881, **14**, 2442; 1882, **15**, 42) proves, however, that his evidence is inconclusive, for whilst phenol and dibromocarbani-*l*ide are the products arising from the decomposition by water of the diazo-carbamide obtained from benzenediazoamino-*p*-bromobenzene, the action of water on the diazo-carbamide from benzenediazoamino-*p*-toluene yields both phenol and *p*-cresol and a viscous product from which only di-*p*-tolylcarbamide can be isolated. The viscous product may and probably does contain diphenylcarbamide, seeing that both phenol and *p*-cresol are formed. If such is the case, the diazoamine reacts with carbonyl chloride in accordance with both formulæ, $\text{C}_6\text{H}_5\cdot\text{N}_2\cdot\text{NH}\cdot\text{C}_7\text{H}_7$ and $\text{C}_6\text{H}_5\cdot\text{NH}\cdot\text{N}_2\cdot\text{C}_7\text{H}_7$. Similar reasoning holds in the case of benzenediazo-*m*-aminobenzoic acid, phenol and *m*-hydroxybenzoic acid being the only substances isolated from the decomposition products of its diazo-carbamide.

The preceding constitution of a mixed diazoamine has been far more satisfactorily established by Goldschmidt and Molinari (*Ber.*,

1888, 21, 2578), by heating equimolecular quantities of the diazoamine and phenylcarbimide in an indifferent solvent, such as benzene. The product is a diazocarbamide, which can be isolated and appears to be an individual substance; it is decomposed by water, yielding a phenol, nitrogen, and a diarylcarbamide, of which one aromatic group is always phenyl, and the other the more negative group of the original diazoamine:



In the preceding year, however, the results of two investigations were published which partly supported and partly opposed Goldschmidt's conclusions. Heumann and Oeconomides (*Ber.*, 1887, 20, 372, 904) found that diazoaminobenzene, when heated in phenol, reacted to form aniline and benzeneazophenol; similarly, *p*-chlorobenzenediazoamino-*p*-toluene gave *p*-chloroaniline and *p*-tolueneazophenol. Benzenediazoamino-*p*-toluene, however, with phenol or resorcinol gave approximately equal quantities of aniline and *p*-toluidine and a mixture of hydroxyazo-compounds. In these reactions, therefore, some mixed diazoamines behave as if constituted in accordance with Goldschmidt's formula, others like mixtures of equal quantities of $\text{ArN}_2\cdot\text{NHAr}'$ and $\text{ArNH}\cdot\text{N}_2\text{Ar}'$. Still more striking is the evidence advanced by Noelting and Binder (*Ber.*, 1887, 20, 3004), who submitted benzenediazoamino-*p*-toluene and other mixed diazoamines to the attack of numerous reagents, and found that they behaved sometimes in accordance with the formula $\text{ArN}_2\cdot\text{NHAr}'$, sometimes in accordance with the formula $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\text{Ar}'$, but generally as a mixture of both forms.

As a result of these and other investigations, two views were current regarding the constitution of mixed aromatic diazoamines, and these have not been materially modified by more recent researches. One view, which does not appear to have been urgently advanced by any single investigator, regards the mixed diazoamines as consisting of the two possible isomerides, $\text{ArN}_2\cdot\text{NHAr}'$ and $\text{ArNH}\cdot\text{N}_2\text{Ar}'$. The other theory, initiated by Goldschmidt, regards the diazoamines as being constituted so that the imino-group is attached to the more negative aromatic group. Reactions in which the diazoamine yields four products of decomposition are attributed to a migration of the iminic hydrogen atom due to the presence of water, alcohol, or an electrolyte, and are explained by an initial addition of water or the like; thus:

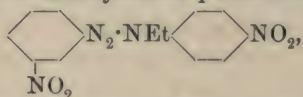


by the elimination of HX, $\text{Ar}\cdot\text{NH}\cdot\text{N}_2\text{Ar}'$ and $\text{ArN}_2\cdot\text{NHAr}'$ may result, and by subsequent decomposition yield each a pair of products. Goldschmidt claimed that the migration of the iminic

hydrogen atom does not occur in indifferent solvents, such as benzene, petroleum, or chloroform, and consequently in such solvents diazoamines behave as individual substances and not as mixtures, and to this cause attributes the success of his phenylcarbimide method of determining the constitution of diazoamines.

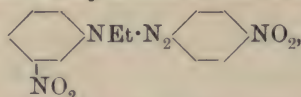
In arriving at this theory, Goldschmidt apparently has overlooked the exhaustive researches in 1886—1895 of Meldola and Streatfeild on alkylated diazoamines. Although alkylation as a method of determining constitution has been viewed in recent years with some suspicion, yet in some instances, for example, the phthaleins and the hydroxyazo-compounds, the problem of the constitution of a substance containing a mobile hydrogen atom has been approached and to a great extent solved by replacing the migratory hydrogen atom by an immobile alkyl group. If, therefore, an alkylated diazoamine can be shown to have a similar constitution to that of its parent substance, Meldola and Streatfeild's researches acquire a new and fundamental significance, and can be utilised directly to prove the untenability of the theory that in a mixed aromatic diazoamine the imino-group is attached to the more negative aromatic nucleus. We have been able to prove the point in question by means of the spectrograph. Meldola and Streatfeild showed that three isomeric *mp'*-dinitrodiazoethylaminobenzenes exist, namely:

I. *m*-Nitrobenzenediazoethylamino-*p*-nitrobenzene,



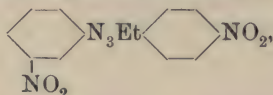
prepared from diazotised *m*-nitroaniline and *p*-nitroethylaniline.

II. *p*-Nitrobenzenediazoethylamino-*m*-nitrobenzene,



from diazotised *p*-nitroaniline and *m*-nitroethylaniline.

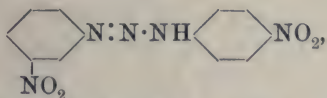
III. *mp'*-Dinitrodiazoethylaminobenzene,



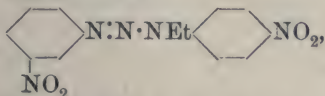
obtained by the direct ethylation of *mp'*-dinitrodiazoaminobenzene.

Isomeride III gives an absorption curve different from those of I and II, and absolutely identical with that of its parent diazoamine, which is thus proved to have a constitution similar to that of isomeride III. The constitution of this isomeride has been practically proved by Meldola and Streatfeild, who find that it can be

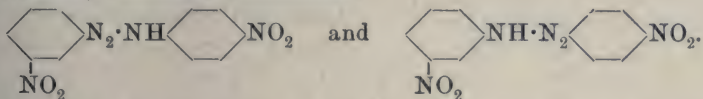
synthesised by heating equimolecular quantities of isomerides I and II in alcohol or benzene. Meldola and Streatfeild regard III as a compound of I and II. For reasons given below we believe it to be an equimolecular mixture of I and II, but for the present purpose this difference of opinion is immaterial, the main point being that III is composed of equal quantities of I and II, either mixed or combined. Now, in the diazoamine under discussion, the *p*-nitrobenzene nucleus is probably the more negative, but whether this is really so does not affect the argument. Assuming that it is, the diazoamine will be represented by the Goldschmidt theory by the formula:



and the directly alkylated derivative, which must possess a similar constitution to that of its parent substance from the spectrometric evidence, will have the formula:



that is, should be identical with isomeride I above. Since experiment shows that the directly alkylated derivative is III above, that is, a mixture of equal quantities of I and II, it follows that the premise is incorrect, and that *mp'*-dinitrodiazoaminobenzene consists of a mixture (or compound) of equal quantities of the two individually unknown isomerides:



Of course, the acceptance of this theory at once renders intelligible the numerous reactions in which a mixed diazoamine yields four products of decomposition. It only remains to explain why the diazoamine at times yields only two products, decomposing as though it consisted entirely of one of the two unknown isomerides. At present it is impossible to advance any argument satisfactorily supported by experimental evidence. The most obvious explanation is the selective attack of the reagent. If one of the two isomerides is attacked at a much greater rate than the other, a transformation of the less susceptible into the more susceptible isomeride must occur in order to preserve the equilibrium ratio at unity, and the diazoamine will decompose almost entirely as though it consisted of one isomeride only. The most important case to which this explanation can be applied is the phenylcarbimide reaction, since

this forms the main foundation of the Goldschmidt theory of the constitution of diazoamines. Goldschmidt attributes the formation of an individual diazocarbamide from phenylcarbimide and a mixed diazoamine in benzene solution to the immobility of the iminic hydrogen atom in an indifferent solvent. Dimroth, however, gives instances (*Annalen*, 1904, **335**, 1) in which the transformation of one tautomeride into another by the migration of a mobile hydrogen atom proceeds much more rapidly in an indifferent solvent than in a hydroxylic solvent. Goldschmidt admits that this is correct in principle, but is not applicable to the particular case of the diazoamines, because one of the isomeric forms is unknown (*Ber.*, 1905, **38**, 1097). Our experiments prove, however, that both forms exist as an inseparable mixture in the mixed diazoamine. The unitary course of the phenylcarbimide reaction, therefore, may very well be due to the selective attack of the reagent, the transformation of one isomeride in the mixed diazoamine into the more susceptible form being facilitated by the indifferent solvent to such a degree that one diazocarbamide is produced only in inappreciable quantities.

It would be premature to dogmatise from the result of the examination of a single triplet of ethers originating from a diazoamine containing aryl groups of not very different character, and we do not unhesitatingly commit ourselves at present to the views advanced above, and the less so in consequence of Pechmann's work on amidines of the type $\text{ArN}:\text{CPh}\cdot\text{NH}\cdot\text{Ar}'$ (*Ber.*, 1895, **28**, 869), which differ from mixed diazoamines by containing the group CPh in place of a nitrogen atom. The compound $\text{C}_6\text{H}_5\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, obtained from benzanilide iminochloride and *p*-toluidine, is identical with $\text{C}_7\text{H}_7\cdot\text{N}:\text{CPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_5$, prepared from benzoyl-*p*-toluidide iminochloride and aniline, but yields by ethylation a mixture of two ethyl derivatives corresponding with the two formulæ given. When Ar and Ar' are different in character, however, the amidines produced by the two methods are still identical, but yield only one ether, indicating an immobility of the hydrogen atom in the amidine. A similar constitution may obtain for mixed diazoamines containing aryl groups of very different character, the imino-group remaining attached to the negative nucleus as in the Goldschmidt theory. This view of the constitution of such diazoamines, which, of course, harmonises well with the chemical behaviour cited above, can be tested spectrometrically, and is receiving our attention.

The derivative obtained by the direct alkylation of a mixed diazoamine has been shown by Meldola and Streatfeild to be composed of equal quantities of the two isomerides, $\text{ArN}_2\cdot\text{NR}\cdot\text{Ar}'$ and $\text{ArNR}\cdot\text{N}_2\cdot\text{Ar}'$, by boiling an alcoholic or benzene solution of

these isomerides for one hour, whereby a product is obtained identical with the directly alkylated diazoamine. The authors regard this product as a compound of the two isomerides, although they found that the molecular weight in benzene by the cryoscopic method agreed with a unimolecular and not a bimolecular formula, a discrepancy which they attribute to dissociation of the compound in the benzene solution. This explanation is untenable, since the compound is produced in boiling benzene, and it is very improbable that it would dissociate in the cold solvent. Mr. T. J. Mander, to whom we proffer our thanks, has determined the molecular weights of several alkylated mixed diazoamines in boiling alcohol and benzene, and has obtained values which are always less than those corresponding with the unimolecular formula. The compound, therefore, does not exist in the solution, and must be produced, if formed at all, at the instant of the deposition of the solid from the solution. To ascertain whether or not a compound is formed, we have determined the melting-point curve of mixtures of *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene and *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene. The curve is of the simple U-shape characteristic of mixtures, and has its minimum at a point corresponding with the mixture of equal quantities of the two isomerides and a temperature identical with the melting point of the substance obtained by the direct ethylation of *mp'*-dinitrodiazoaminobenzene. This evidence, combined with that furnished by the cryoscopic and the ebullioscopic methods of determining the molecular weight, proves that the directly ethylated substance is a solid solution of equal quantities of the two isomerides mentioned above.

EXPERIMENTAL.

mp'-Dinitrodiazoaminobenzene.—This compound was prepared in the usual way from *m*-nitroaniline and *p*-nitrobenzenediazonium chloride in the presence of sodium acetate. The crude substance melted at 214°; after crystallisation from a mixture of equal volumes of alcohol and toluene, the melting point was 218–219°. Since Meldola and Streatfeild give the melting point as 212–212.5° (Trans., 1889, 55, 416), the substance was again dissolved in boiling alcohol and toluene, filtered while still hot (precipitate A), again when cold (precipitate B), and yet again after concentrating the mother liquor (precipitate C). The melting points of A, B, C respectively were 220°, 212.5–213°, 219–220°. After recrystallisation from the same solvent, the melting points were 231–232°, 231–232°, 230–231°, in a bath previously heated to 180°. After a third recrystallisation, the melting points were 231–232°, 231–232°, 228°. In all cases the substance decomposes

at the melting point. The three samples all gave the same orange-red colour in alcoholic sodium hydroxide, and dissolved without change of colour in concentrated sulphuric acid, forming solutions which ultimately became colourless. The melting point of *pp'*-dinitrodiazoaminobenzene is given by Hantzsch as 233° (decomp.), a value which we have confirmed. The melting point of a mixture of approximately equal quantities of this compound and our *mp'*-isomeride melted at 208—211° (decomp.).

mp'-Dinitrodiazoethylaminobenzene was prepared by heating the diazoamine with alcoholic potassium hydroxide and ethyl iodide on the water-bath for eight hours, and twice recrystallising the product from alcohol. It melted at 152—153°, dissolved in alcoholic sodium hydroxide without change of colour, and gave a solution in concentrated sulphuric acid, which became colourless after a few hours.

m-Nitrobenzenediazoethylamino-*p*-nitrobenzene and *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene were prepared from diazotised *m*-nitroaniline and *p*-nitroethylaniline and diazotised *p*-nitroaniline and *m*-nitroethylaniline respectively, and were recrystallised from alcohol and toluene until the melting points were constant at 174.5—174.8° and 188.5—188.7° respectively; the substances dissolved in alcoholic sodium hydroxide without change of colour, and gave solutions in concentrated sulphuric acid, which ultimately became colourless.

The absorption curves of *mp'*-dinitrodiazoaminobenzene and of the three ethylated isomerides are shown in Fig. 1. The curves of the parent diazoamine and of its directly ethylated derivative are identical throughout. The curves of the other two isomerides, although naturally very similar to, are quite distinct from, that of the directly ethylated isomeride. A comparison of the three curves, particularly in the neighbourhood of oscillation frequencies 3200 to 3600, indicates that the curve of the directly ethylated diazoamine is very much what would be expected if the substance is a mixture of the other two isomerides. The most important result, however, is the proof of the similarity of the constitutions of *mp'*-dinitrodiazoaminobenzene and its directly ethylated derivative.

To obtain the melting-point curve of *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene and *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene shown in Fig. 2, it is necessary that the heating of the different mixtures shall be as uniform and under as nearly the same conditions as possible, for it is well known that the apparent melting point of a diazoamine can be raised many degrees by rapid heating. Intimate mixtures of the two isomerides were obtained by making two solutions in benzene distilled over sodium:

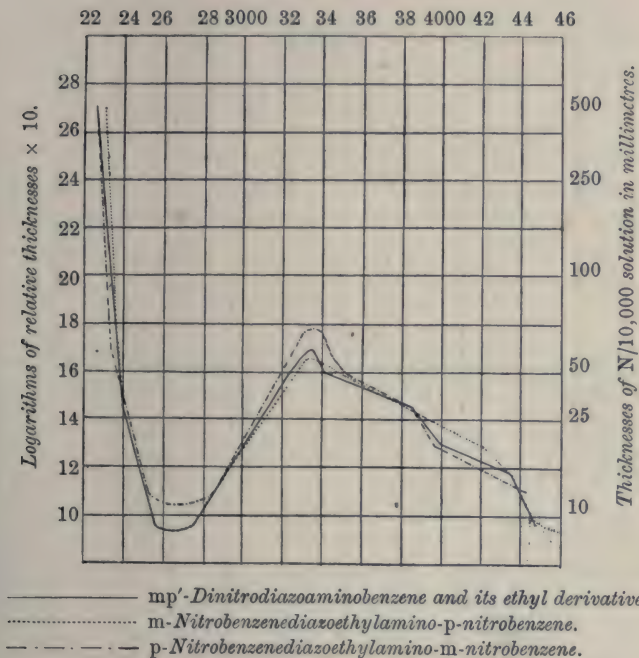
A. Containing 0.1575 gram of *m*-nitrobenzenediazoethylamino-*p*-nitrobenzene in 250 c.c.

B. Containing 0.1575 gram of *p*-nitrobenzenediazoethylamino-*m*-nitrobenzene in 250 c.c.

Mixtures of different volumes of these two solutions were evaporated on the water-bath, the residue was detached from the basin, finely powdered, and transferred as completely as possible to capillary tubes about 2 mm. in diameter and about 15 cm. long.

FIG. 1.

Oscillation frequencies.

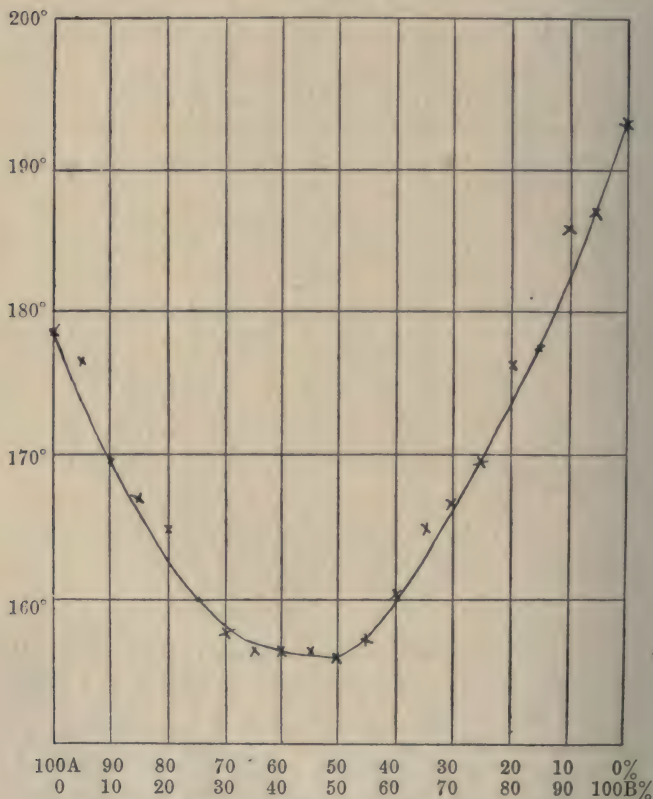


These tubes were attached to a thermometer 70 cm. in length, having a range from 100° to 200°, graduated in tenths of a degree. The bulb of the thermometer was immersed in sulphuric acid contained in the outer jacket of a Victor Meyer vapour density apparatus. The temperature of the acid was raised to 100°, then the capillary tube was affixed to the thermometer, and the temperature was raised fairly rapidly to within 10° of the melting point of the preceding mixture; the rate of heating was then adjusted so that the temperature rose 1° per minute.

The following table gives the data from which the curve in Fig. 2 is plotted:

C.c. of A.	C.c. of B.	Corrected melting point.	C.c. of A.	C.c. of B.	Corrected melting point.
20	0	178.5—178.8°	9	11	157.2°
19	1	176.6	8	12	160.2—161.6
18	2	169.1—169.8	7	13	164.5—165.5
17	3	166.9—167.2	6	14	166.8—167.4
16	4	164.5—165.4	5	15	169.1—169.8
15	5	159.6—160.4	4	16	176.1—176.9
14	6	157.3—157.5	3	17	177.6—177.9
13	7	156.1—156.5	2	18	185.9—186.1
12	8	156.4—156.9	1	19	186.9—187.2
11	9	156.3—156.9	0	20	193.2—193.4
10	10	155.4—156.2			

FIG. 2.



A = *m*-Nitrobenzenediazoethylamino-*p*-nitrobenzene.

B = *p*-Nitrobenzenediazoethylamino-*m*-nitrobenzene.

It will be noticed that mixtures containing from 65 to 50 per cent. of A melt at only slightly different temperatures, but there

is not the slightest doubt that the equimolecular 50 per cent. mixture has the lowest melting point, which is the same as that of the substance obtained by the ethylation of *mp'*-dinitrodiazoaminobenzene.

In order to see whether a compound of the two isomerides is formed under the conditions mentioned by Meldola and Streatfeild, mixtures of A and B were heated under a reflux condenser for one hour on the water-bath; the benzene was then evaporated, and the melting points of the residues determined as above. The results tabulated below show that the melting points are practically unchanged by this treatment:

C.c. of A.	C.c. of B.	Corrected melting point.	C.c. of A.	C.c. of B.	Corrected melting point.
20	0	178.2—178.3°	8	12	160.4—160.9°
15	5	159.3—159.7	5	15	168.8—169.8
12	8	156.3—156.8	0	20	192.0—192.6
10	10	155.1—155.7			

In conclusion, we wish to express our thanks to the Research Fund Committee of the Chemical Society for a grant by which the expense of this investigation has been largely defrayed.

EAST LONDON COLLEGE.

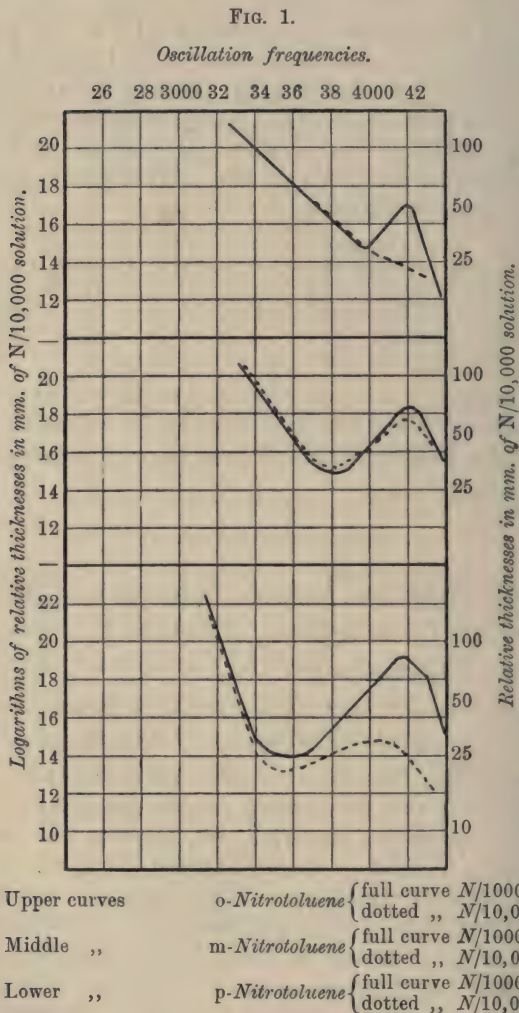
LIX.—*The Relation between Absorption Spectra and Chemical Constitution. Part XIV. The Aromatic Nitro-compounds and the Quinonoid Theory.*

By EDWARD CHARLES CYRIL BALY, WILLIAM BRADSHAW TUCK, and
EFFIE GWENDOLINE MARSDEN.

It has been shown (Trans., 1905, **87**, 1332) that the introduction of the nitro-group into the benzene nucleus produces a very marked effect on the absorption spectrum, for, whereas the parent hydrocarbon shows a number of closely situated absorption bands, nitrobenzene is characterised by a very strongly marked general absorption with only a very shallow band.* The view was put forward that this change is due to the fact that the strong residual affinity of the nitro-group restrains the vibrations of the benzene ring. If, now, a second group be introduced, and this group be of the so-called positive type, that is to say, one with directing influence to the ortho- and para-positions, the tendency of the nitro-group to restrain the benzene ring vibrations is more or less eliminated.

* The presence of this shallow band has only recently been detected with a large spectrograph in the case of an alcoholic solution. Nitrobenzene in petroleum solution does not show the band.

We have now examined a number of aromatic compounds derived from nitrobenzene, and we find that these substances all show more or less pronounced absorption bands, the depth and position



of which depend on the character of the substituent group or groups.

The simplest cases are those of the three nitrotoluenes, where the second group is the not very strongly marked electropositive methyl. The absorption curves of the ortho-, meta-, and para-isomerides are shown in Fig. 1 (full curves), and they all three

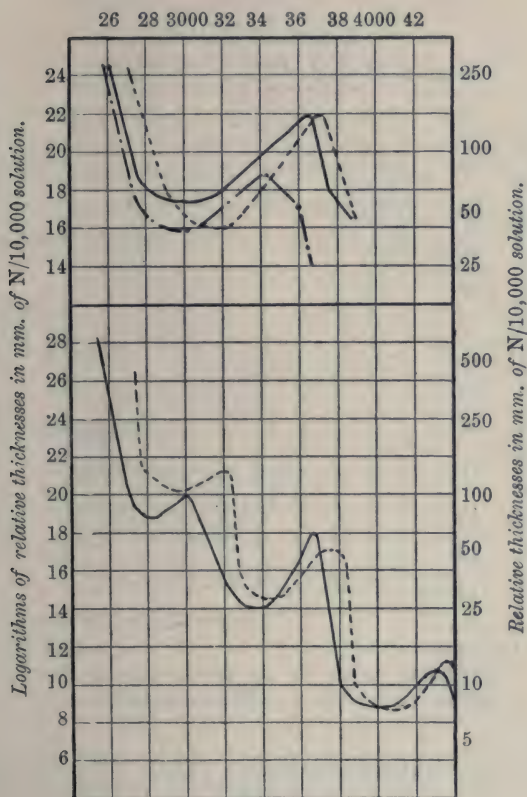
show well-marked absorption bands. The differences between the absorption as shown by the full and dotted curves will be discussed below under the section dealing with the effect of the solvent. The

FIG. 2.

Upper Curves.

Full curve	<i>α-Nitronaphthalene in alcohol.</i>
Dotted curve	„ „ <i>light petroleum.</i>
Dot and dash curve	„ „ <i>benzene.</i>

Oscillation frequencies.



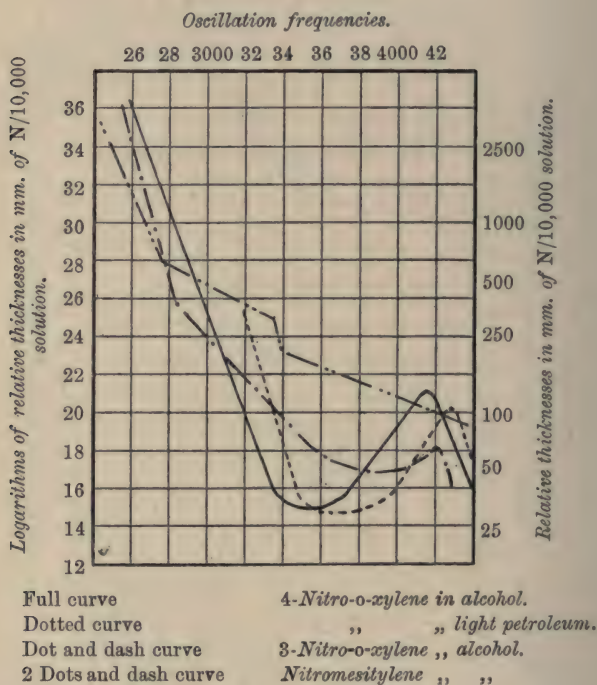
Lower Curves.

Full curve	<i>β-Nitronaphthalene in alcohol.</i>
Dotted curve	„ „ <i>light petroleum.</i>

two mononitronaphthalenes also show well-marked absorption bands, as can be seen on reference to the full curves in Fig. 2. The α -compound shows one band, whilst the β -isomeride has three. We

have also examined the absorption of the two mononitro-*o*-xylenes, the curves being shown in Fig. 3. Here again well-marked bands are exhibited. It is noticeable in a comparison of 4-nitro-*o*-xylene with the nitrotoluenes that the former compound possesses a much deeper band than the latter. Clearly, therefore, the two methyl groups in the former substance exert a greater counteracting influence against the restraint of the nitro-group than the single methyl group in the nitrotoluenes. At the same time, the relative position of the nitro-group and the methyl groups has a considerable

FIG. 3.

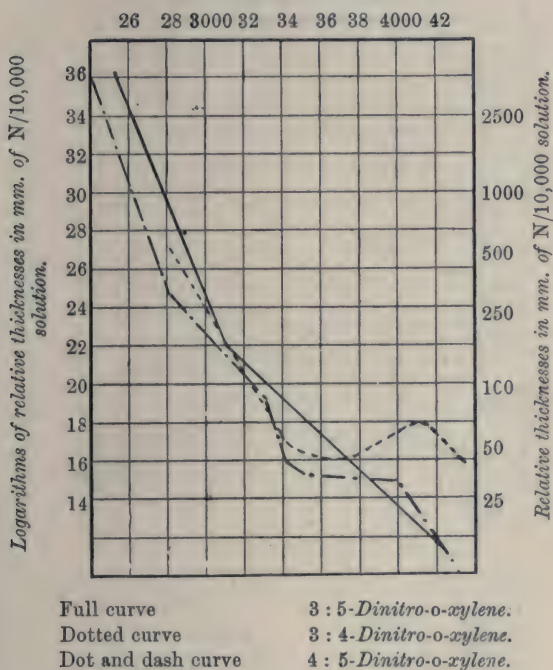


bearing on their mutual influence. Thus, in the nitrotoluenes the ortho-isomeride shows an absorption which is the shallowest and farthest from the red, whilst the band of the para-isomeride is the deepest and nearest the red. The small band given by 3-nitro-*o*-xylene is therefore attributable to the fact that the two methyl groups and the nitro-group are adjacent to one another. This is still more strikingly exemplified in the case of nitromesitylene, which shows no band at all. This follows readily from the fact that the three methyl groups are all in the meta-positions with

respect to one another; as has been previously shown, mesitylene exhibits very small absorption owing to this fact, and therefore the three methyl groups will not be able to overcome the restraint of the nitro-group, because they of themselves also tend to restrain the vibrations of the ring.

In the case of the two nitronaphthalenes the restraining influence of the nitro-group on the one ring is eliminated by the second ring, with the result that very well-marked absorption bands are produced which are nearer the red than those of naphthalene itself. In both

FIG. 4.

Oscillation frequencies.

these compounds, especially in the α -isomeride, the absorption bands are sufficiently near to the red for the substances to be visibly coloured.

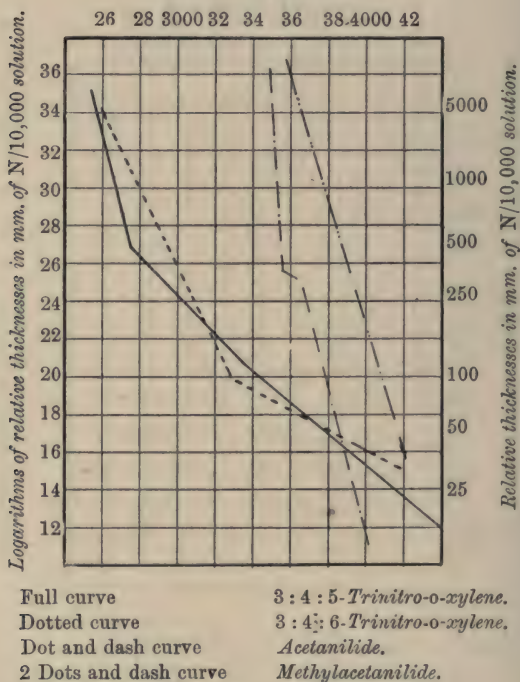
If two nitro-groups are substituted in one benzene ring, then of course the influence of the positive groups must be greater in order to produce a counteracting effect equal to that in a mono-nitro-compound. This is well shown in the case of the two dinitro-*o*-xylenes (Fig. 4), of which the 3:4-dinitro-isomeride shows a very shallow band, whilst in the 4:5-dinitro-isomeride the

absorption band has just disappeared. Still more pronounced is this the case in trinitro-compounds, for both the 3:4:5- and the 3:4:6-trinitro-*o*-xylenes (Fig. 5) show only general absorption without even the attempt to show the band evidenced by the 4:5-dinitro-compound.

The definite conclusion can therefore be drawn that if the restraining influence of the nitro-group in nitrobenzene is counteracted by the introduction of one or more so-called positive groups,

FIG. 5.

Oscillation frequencies.



isorropesis is set up, and one or more absorption bands are produced. Further, the position and persistence of this absorption are determined by the amount that the restraining influence of the nitro-group is eliminated as a result of the introduction of the positive groups, and also by the position of the absorption band of the non-nitrated compound.

As a further test, the spectra of mono- and di-nitrofluorene were examined. The first of these (I) is practically colourless, having only a slight cream colour, while the dinitro-compound (II) is

strongly yellow. These two compounds afford a rigid test of the above conclusion, for the mononitro-compound should show a

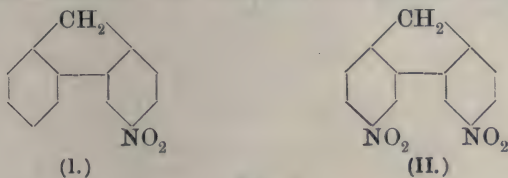
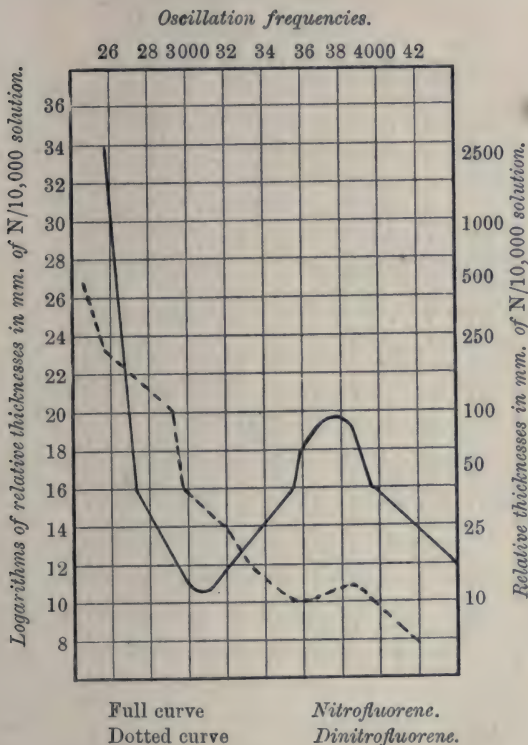


FIG. 6.



strong absorption band, whilst the dinitro-compound should show very little or no evidence of a band, since both phenyl groups have their motions restrained by a nitro-group. The curves are shown in Fig. 6, and, as can be seen, the results are exactly as was predicted.

We have also examined the absorption spectra of nitrobenzene substituted by other groups than methyl, as, for example, the nitrocinnamic ethyl esters. Their absorption curves are shown in Fig. 7, and here there is a deep absorption band at $1/\lambda = 3350$ in the para-isomeride. The meta-compound shows a band at $1/\lambda = 3850$, and a step-out at $1/\lambda = 3200$, whilst the ortho-isomeride

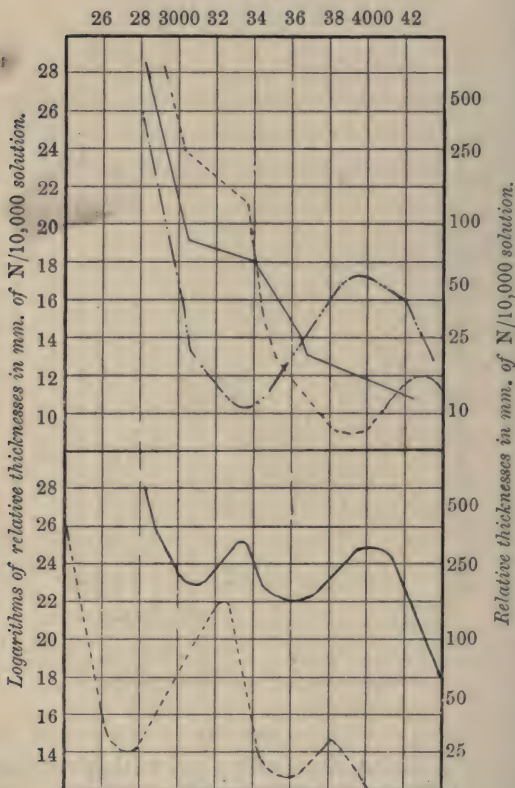
only shows a step-out at $1/\lambda = 3200$. There is also here a progressive effect of the $\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{Et}$ group from the ortho- to the para-position as in the nitrotoluenes.

FIG. 7.

Upper Curves.

Full curve	<i>o</i> -Nitrocinnamic ester.
Dotted curve	<i>m</i> -Nitrocinnamic ester.
2 Dots and dash curve	<i>p</i> -Nitrocinnamic ester.

Oscillation frequencies.



Lower curves.

Full curve	<i>o</i> -Coumaric acid in alcohol.
Dotted curve	<i>o</i> -Coumaric acid in alcoholic NaOEt.

If now the substituent group be very strongly positive, it is evident from what has gone before that the absorption band will tend to be nearer the red, for it must be remembered that the

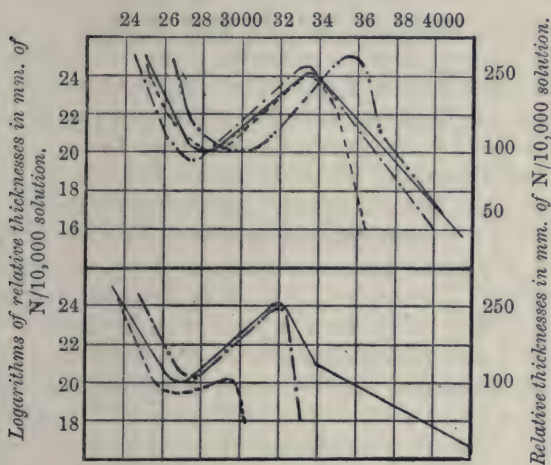
absorption band of benzene substituted by a strong positive group, such as OMe or OEt, is generally more persistent and nearer the red than that of the xylenes or toluene. This is very strikingly observed in the case of nitroquinol dimethyl ether, the absorption of which in alcoholic solution is shown in Fig. 8. The head of the absorption band is now at $1/\lambda = 2800$, which is distinctly nearer the red than the compounds previously described. The

FIG. 8.

Upper Curves.

Full curve	<i>Nitroquinol dimethyl ether in alcohol.</i>		
Dotted curve	"	"	<i>benzene.</i>
Dot and dash curve	"	"	<i>chloroform.</i>
2-Dots and dash curve	"	"	<i>light petroleum.</i>

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitroquinol dimethyl ether in water.</i>		
Dotted curve	"	"	<i>aniline.</i>
Dot and dash curve	"	"	<i>pyridine.</i>

compound, as is well known, has a strong yellow colour, and its solution in alcohol is also yellow. It is evident that the absorption of this compound, and therefore its colour, is capable of the same explanation as that put forward for the compounds previously described, that is to say, it is due to the isorropesis between the residual affinity of the nitro-group and that of the quinol dimethyl ether residue. The absorption spectrum of the quinol dimethyl ether has already been described (*Trans.*, 1905, **87**, 1353), and shows a very deep absorption band with its head at about $1/\lambda = 3445$.

The question now arises as to whether the above explanation of the absorption and colour of the substituted nitro-compounds should not be perfectly general and include all the substances of this type, such as the nitroanilines and the nitrophenols. In the last two classes of compounds the colour and absorption has been attributed to their existing in the quinonoid configuration. Indeed, one of us, in conjunction with Dr. Stewart and Dr. Edwards (Trans., 1906, **89**, 514), put this forward as the interpretation of the results obtained from the spectroscopic observation of the nitrophenols and the nitroanilines. In the case of the former it was judged that the sodium salts have the quinonoid formula owing to their absorption bands being so much nearer to the red than those of the free substances. On the other hand, from the results described in this paper, it would seem more probable that another explanation of their absorption spectra is preferable, an explanation similar to that given above for the nitro-compounds, which clearly cannot exist in a simple quinonoid form. On these lines, the absorption bands of the nitroanilines, for example, would be due to the isorropesis between the nitro-group and the aniline residue. These bands would necessarily be very near the red owing to the fact that the absorption band of aniline is high up the spectrum ($1/\lambda=3500$). As regards the nitrophenols and their sodium salts there should be a considerable difference in their absorption on account of the great difference between the absorption of phenol and of sodium phenoxide. The absorption spectrum of phenol (Trans., 1905, **87**, 1351) shows a band with its head at $1/\lambda=3680$, whilst sodium phenoxide shows a band with head at $1/\lambda=3420$. In nitrophenols, therefore, the isorropesis is between the free period of the nitro-group and a residue with bands at $1/\lambda=3680$, whilst in the sodium nitrophenoxides the isorropesis is between the nitro-group and a residue with a band at $1/\lambda=3420$. Clearly, therefore, the absorption of the latter compound should be much nearer the red.

We thought it worth while, therefore, to undertake anew the investigation of these compounds with the help of the new and much better spectrograph than was available at the time of the previous investigation. We will deal first with the nitroanilines and their alkyl derivatives. In Fig. 9 are shown the curves of 3-nitro-*p*-toluidine, its mono- and di-methyl, and also the acetyl and acetylmethyl derivatives. The free base shows a deep absorption band with its head at about $1/\lambda=2400$, the monomethyl derivative a band with head at $1/\lambda=2350$, whilst the head of the dimethyl compound lies at $1/\lambda=2270$. While it may be urged that the absorption of the free base and the monomethyl derivative is due to their existing in the quinonoid form, it is

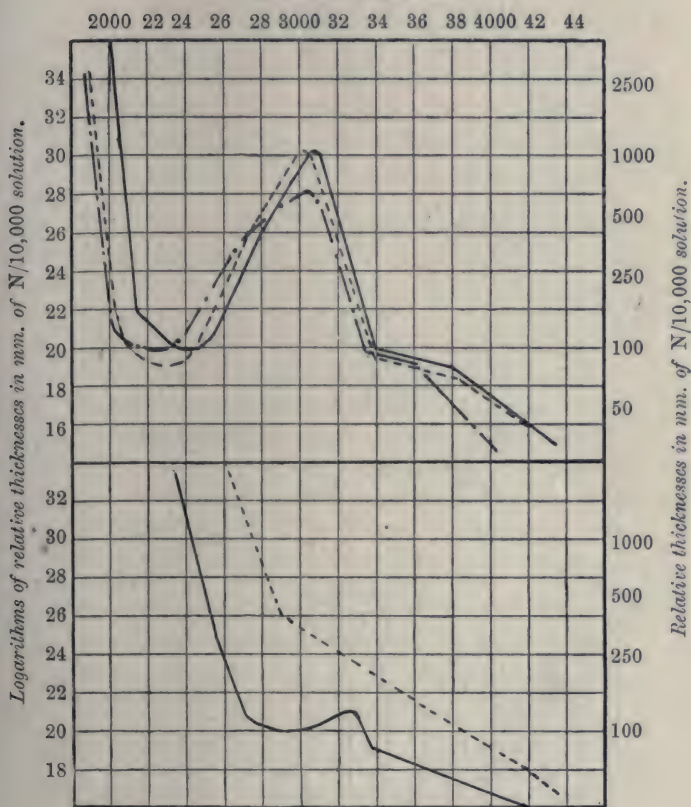
difficult to see how the dimethyl compound can exist in this form, and yet the absorption of all three is almost identical. The only

FIG. 9.

Upper curves.

Full curve	<i>Nitro-p-toluidine.</i>
Dotted curve	<i>Nitromethyl-p-toluidine.</i>
Dot and dash curve	<i>Nitrodimehyl-p-toluidine.</i>

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitroaceto-p-toluidide.</i>
Dotted curve	<i>Nitromethylaceto-p-toluidide.</i>

difference between them is the slight shift of the band towards the red accompanying the introduction of the methyl groups. In connexion with this, it is important to note that the band of

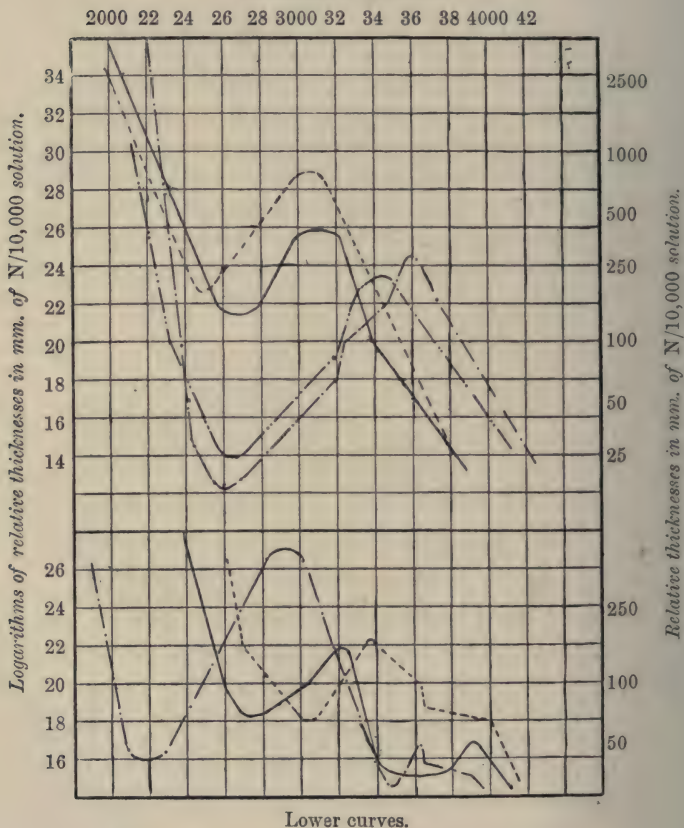
aniline also shifts towards the red when the substance is methylated. The heads of the bands of aniline, methylaniline, and

FIG. 10.

Upper curves.

Full curve	<i>m</i> -Nitroaniline.
Dotted curve	<i>m</i> -Nitrodimethylaniline.
Dot and dash curve	<i>p</i> -Nitroaniline.
2-Dots and dash curve	<i>p</i> -Nitrodimethylaniline.

Oscillation frequencies.



Lower curves.

Full curve	<i>Nitro-p</i> -cresol in alcohol.
Dotted curve	<i>Nitro-p</i> -cresetole in alcohol.
Dot and dash curve	<i>Nitro-p</i> -cresol in alcoholic NaOEt.

dimethylaniline lie at $1/\lambda = 3510$, 3450 , and 3430 respectively. It follows that the bands of the nitro-compound will also shift when the latter is methylated.

The reduction in the absorption arising from the decrease in the residual affinity of the amino-group caused by the introduction of the acetyl group and the acetyl and methyl groups is well shown in the two remaining curves. This is exactly analogous to the decrease in the absorption of aniline caused by the introduction of the acetyl group and the acetyl and methyl groups, as shown by the curves in Fig. 5.

The absorption of *m*- and *p*-nitroanilines compared with that of their dimethyl derivatives is shown in Fig. 10. Exactly the same applies here as in the case of the *o*-nitroamino-compound just described. There is no difference of any moment between the free compounds and the dimethyl derivatives. The conclusion, therefore, is forced upon us that the same explanation of the colour and absorption must be given in each. A simple quinonoid structure is ruled out in the case of the dimethyl compounds, and hence we are compelled to abandon it in the case of the parent substances.

As regards the nitrophenols, the same explanation without doubt is applicable to the para-isomeride as to the compounds already described, for whilst *p*-nitrophenol and *p*-nitroanisole have the same absorption (the bands of anisole and phenol are in the same spectral region), the band of sodium *p*-nitrophenoxide is shifted considerably towards the red. This shift, however, is due to the shift in the absorption band towards the red when sodium hydroxide is added to a phenol solution. In the case of the *o*-nitrophenols, however, the matter is complicated by the fact that in the original paper the spectrum of *o*-nitroanisole differed from that of *o*-nitrophenol.

In order to elucidate this anomaly, we have examined the spectra of *o*-nitrophenol, *o*-nitroanisole, and *o*-nitrophenetole in various solvents, and find that the difference is mainly due to the effect of the solvent. As previously referred to, the influence of the solvent is very remarkable in the case of the nitro-compounds, and this influence will be discussed more fully below. In the original paper, *o*-nitrophenol was shown to have two bands; these are shown in the full curve in Fig. 11, which represents the absorption of an alcoholic solution of this compound. The solution in light petroleum, however, only shows one band—the one nearer the red, whilst the second band has shrunk to a step-out. *o*-Nitroanisole in light petroleum solution also shows one absorption band like the parent substance in the same solvent, but a little nearer the shorter wave-lengths. In alcoholic solution *o*-nitroanisole only shows evidences of the one band nearer the red. This band is shallow, and was only detected with the new instrument. *o*-Nitro-

phenetole shows the same shallow band and also a step-out where the second band should appear.

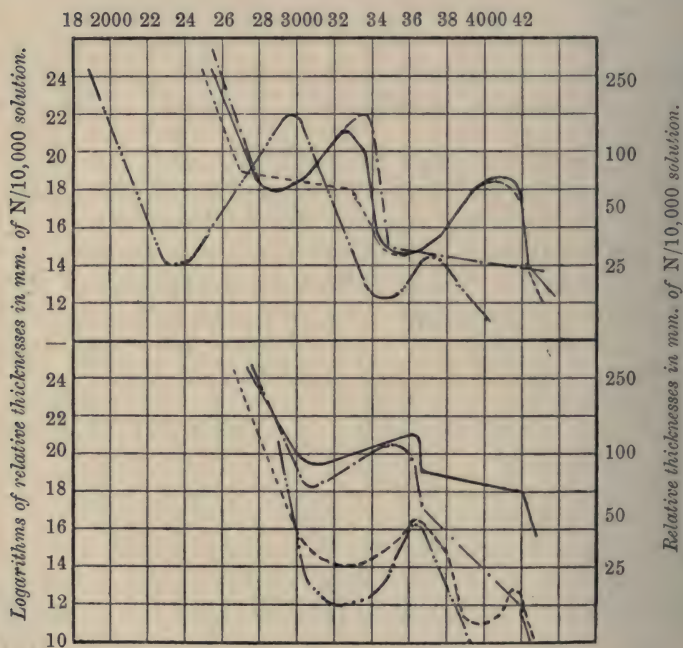
The solution of *o*-nitrophenol in water is different, for the band nearer the red has shrunk to a step-out, whilst the other band is

FIG. 11.

Upper curves.

Full curve	<i>o</i> -Nitrophenol in alcohol.
Dotted curve	" " water.
Dot and dash curve	" " light petroleum.
2-Dots and dash curve	" " alcoholic NaOEt.

Oscillation frequencies.



Lower curves.

Full curve	<i>o</i> -Nitroanisole in alcohol.
Dotted curve	" " light petroleum.
Dot and dash curve	" " alcohol.
2-Dots and dash curve	" " light petroleum.

well marked. Now, *o*-nitrophenol in aqueous solution of the strength dealt with ($N/1000$) is presumably considerably ionised, and, further, this ionisation must be less in alcoholic solution and negligible in light petroleum solution. It would seem from this and

from a comparison with the curves of the ethers that the ionisation of the nitrophenol causes the band nearer the red to shrink, while in the non-ionised substance this band is well marked, while the band farther from the red is decreased.

The absorption of sodium *o*-nitrophenoxide is given in Fig. 11, and shows the first band well marked and the second band very shallow. The change in the absorption when the parent substance is converted into its sodium salt is simply a shift of both absorption bands nearer to the red. As was pointed out above, a shift of this character is bound to take place, because the absorption band of phenol also undergoes a similar shift when sodium hydroxide is added to the solution. The explanation of the absorption of the nitrotoluenes and other compounds advanced above meets this case equally well, and there seems absolutely no reason to assume a radical change in structure such as quinonoid formation in order to explain this shift in the absorption without any change in the type.

Now, owing to the presence of a considerable excess of sodium ethoxide in the solution, it is very improbable that the sodium *o*-nitrophenoxide is ionised to any considerable extent. This is in agreement with the observations, because the ionised or partly ionised nitrophenol in water shows a tendency on the part of the longer wave-length absorption band to shrink, whilst the second band is well marked, the reverse effect being produced when the nitrophenol is dissolved in light petroleum. The sodium salt (in presence of excess of sodium ethoxide in alcoholic solution) is analogous to the latter case, for the shorter wave-length band is decreased, while the other is relatively very deep.

In order not to base our conclusions on one single *o*-nitrophenol, we have examined also *m*-nitro-*p*-cresol and its ethyl ether (Fig. 10), and the results are identical with those of *o*-nitrophenol. The *m*-nitro-*p*-cresetole shows a band at $1/\lambda = 3050$ and a step-out at about $1/\lambda = 3850$; the parent substance in alcohol shows the first band at $1/\lambda = 2800$, and the second band at $1/\lambda = 3650$, whilst in the presence of sodium ethoxide the two bands are shifted to $1/\lambda = 2200$ and $1/\lambda = 3500$ respectively. In aqueous solution the absorption is quite analogous to the case of *o*-nitrophenol, for the shorter wave-length band is increased in persistence, whilst the other one is decreased to a step-out.

We have also repeated the original examination of *m*-nitrophenol and compared it with *m*-nitrophenetole. As the curves on Fig. 12 show, the relation between the free compound, its sodium salt, and its ethyl ether is the same as in the case of the ortho-isomeride, and the same explanation holds good. The para-compounds have

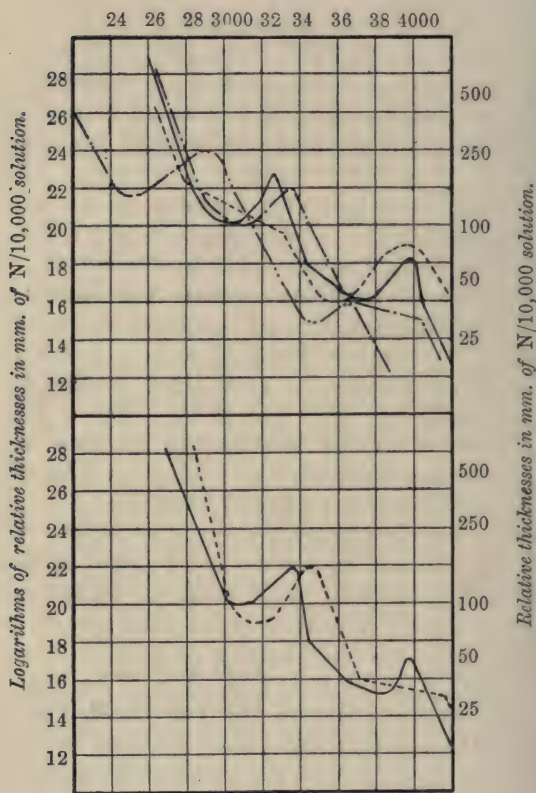
also been examined, and their absorption curves are shown in Fig. 13. Exactly the same shifts of the absorption bands may

FIG. 12.

Upper curves.

Full curve	<i>m</i> -Nitrophenol in alcohol.
Dotted curve	„ „ water.
Dot and dash curve	„ „ light petroleum.
2 Dots and dash curve	„ „ alcoholic NaOEt

Oscillation frequencies.



Lower curves.

Full curve	<i>m</i> -Nitrophenetole in alcohol.
Dotted curve	„ „ light petroleum.

be noticed here, the only difference being that one deep band is exhibited in the place of the two in the *o*- and *m*-isomerides.

An interesting point may be mentioned here in reference to the

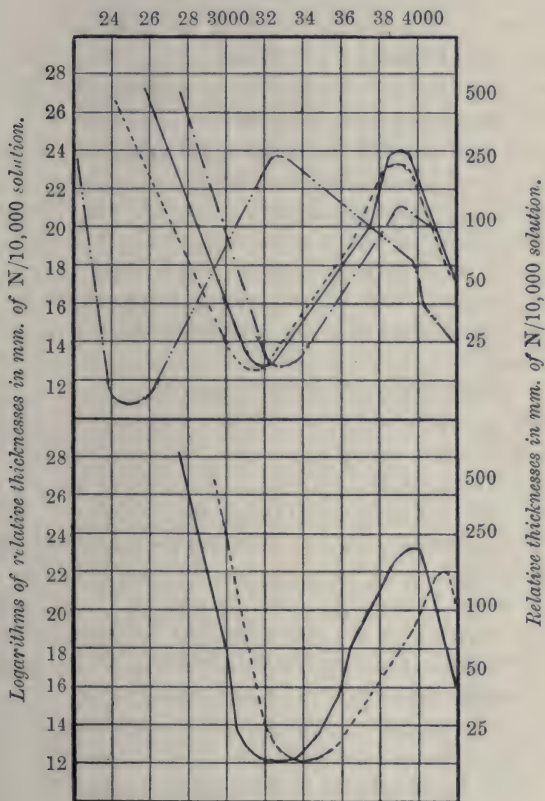
amino- and the $\cdot\text{ONa}$ groups. It appears from the absorption of aniline and sodium phenoxide that the residual affinity of these

FIG. 13.

Upper curves.

Full curve	<i>p</i> -Nitrophenol in alcohol.
Dotted curve	" " water.
Dot and dash curve	" " light petroleum.
2 Dots and dash curve	" " alcoholic NaOEt.

Oscillation frequencies.



Lower curves.

Full curve	<i>p</i> -Nitrophenetole in alcohol.
Dotted curve	" " light petroleum.

two groups is very nearly the same, for the heads of the bands of the two compounds are in the same position. The analogy between these two groups has often been noticed by us in comparing the

spectra of compounds containing first one and then the other group. The resemblance between the nitroanilines and the corresponding sodium nitrophenoxides is very striking.

Perhaps one of the most important arguments against a quinonoid configuration for the nitroanilines and nitrophenols is to be found in the fact that the absorption bands of all the compounds described in this paper appear at the same concentration of solution. This is the case whether the compound can or cannot exist in a quinonoid form. It must be remembered that the absorption spectrum of *p*-benzoquinone shows its isorropesis band at a concentration of $N/10$, whilst all the nitro-compounds show their bands in $N/1000$ -solution. Moreover, the shape of the absorption curve of quinone and those of the nitro-compounds is quite different. It therefore seems in the highest degree improbable that the shift in the absorption bands, which takes place without any change of type when the nitrophenols are converted into their sodium salts, is due to a radical change of structure, as is demanded by the quinonoid hypothesis. As collateral evidence it may be pointed out that the sodium salts of the nitrophenols are extremely similar in their absorption to the nitroanilines, and these again to their dimethyl derivatives. The latter cannot be written in a simple quinonoid form, and therefore the conclusion follows that none are in the quinonoid form.

If the theory put forward in this paper is correct, it is evident that it must be applicable to all the compounds obtained by substituting a positive group into benzaldehyde, benzoic acid, and acetophenone, for the $\cdot\text{CHO}$, $\cdot\text{CO}_2\text{H}$, and $\cdot\text{COMe}$ groups are quite analogous to the nitro-group in that they tend to restrain the motions of the benzene ring. Many such compounds have been examined, and some have been previously published (aminoacetophenones, aminobenzaldehydes), and the results of the investigation are analogous to those given above for the nitro-compounds.

Similarly, of course, the same explanation must be applicable to compounds derived from benzene by the substitution of a hydroxyl group and any other group which carries residual affinity. For example, in coumaric acid, where the group $\cdot\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$ is in the ortho-position with respect to the hydroxyl groups, absorption bands should appear, which should shift towards the red on the addition of an excess of sodium hydroxide. The curves obtained both with and without alkali are shown in Fig. 7, and, as can be seen, the free acid shows two absorption bands, which are shifted towards the red in strongly alkaline solution. In cinnamic acid, where the isorropesis takes place between the residual affinities of the phenyl group and the unsaturated side-chain, the absorption

band has its head at $1/\lambda = 3600$. In *o*-hydroxycinnamic acid there are two bands with heads at $1/\lambda = 3100$ and 3650 , whilst in the disodium compound the two bands have their heads at $1/\lambda = 2750$ and 3600 . The shift of the bands in the latter is sufficiently large for the substance to be strongly yellow. It is true that in the case of coumaric acid a quinonoid formula can be written, but there is considerable inherent improbability of this change taking place, for it necessitates the postulation of there being a greater attraction between sodium and carbon than between sodium and oxygen. On the other hand, the shift in the absorption when phenol is converted into sodium phenoxide is sufficient to cause the shift when the substituted compound is so treated. A striking analogy between the amino- and ONa groups is to be found in the fact that the coumaric acid in strongly alkaline solution fluoresces with the same yellowish-green colour as *o*-aminocinnamic acid.

There seems therefore to be very strong evidence against a quinonoid explanation of the absorption and colour of the nitrophenols and nitroanilines. It would seem, indeed, that this theory is quite unnecessary. The explanation advanced in this paper, an explanation based on the play of forces between the residual affinities in the various intramolecular groups, has the great advantage in that it embraces all the disubstituted benzene compounds with two dissimilar substituents whether or no a quinonoid configuration is possible. This explanation satisfies all the facts that have been observed, which the quinonoid theory does not, as, for example, the very small change in the absorption when a nitroaniline is methylated, and that the formula of a true quinone (*p*-benzoquinone) is of an absolutely different type.

We have also investigated the mononitro-derivatives of benzylideneaniline. These compounds are interesting, for when the nitro-group is substituted in the benzene residue a simple quinonoid structure is possible, but in the isomeric benzylidenenitroanilines this is not the case. A comparison of the absorption of these compounds shows that they are all strikingly similar, there being, however, slightly more marked absorption bands in the benzylidenenitroanilines than in the nitrobenzylideneanilines, that is to say, those compounds which can exist in the quinonoid form show rather less marked absorption than those which cannot do so. It appears to us that these substances afford very strong evidence against the quinonoid hypothesis. The absorption curves compared with that of benzylideneaniline itself are shown in Fig. 14.

During the progress of this investigation a very interesting paper has appeared by Buttle and Hewitt (*Trans.*, 1909, **95**, 1755), in which the constitution of the di- and tri-nitrophenols is discussed.

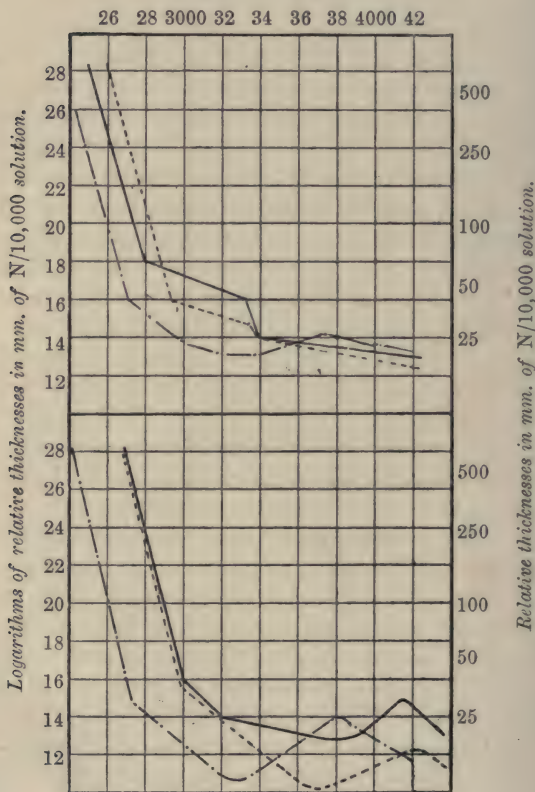
Buttle and Hewitt, basing their arguments largely on the results obtained in the original paper (Trans., 1906, **89**, 514), attribute a para-quinonoid structure rather than an ortho-one to the sodium

FIG 14.

Upper curves.

Full curve	<i>o</i> -Nitrobenzylideneaniline.
Dotted curve	<i>m</i> -Nitrobenzylideneaniline.
Dot and dash curve	<i>p</i> -Nitrobenzylideneaniline.

Oscillation frequencies.



Lower curves.

Full curve	<i>Benzylideneaniline.</i>
Dotted curve	<i>Benzylidene-m-nitroaniline.</i>
Dot and dash curve	<i>Benzylidene-p-nitroaniline.</i>

salt of 2:4-dinitrophenol. On the other hand, there is another interpretation to be given to their results, and one which is more satisfactory than the one they give.

In the first place, Buttlet and Hewitt assume that the absorption spectra of the ionised di- and tri-nitrophenols would be those of the *aci*-forms of these compounds. This, however, is not the case as far as the ortho-nitrophenol is concerned, and it would seem worth while that the absorption spectra of these substances in aqueous solution should be examined. It appears from the curves of the two dinitrophenols that there is evidence of a second band at about $1/\lambda = 3900$, which renders the compounds similar to *o*-nitrophenol itself. We would therefore expect the aqueous solution to show this second band more fully developed at the expense of the first band. Again, our results with the solutions of the nitrophenols in light petroleum solution show that the spectrum of the non-ionised compound can be readily obtained in this way. There is no doubt also that considerable importance is to be derived from a comparison of the absorption of picric acid and its ether dissolved in this solvent.

The theory that we have advanced, however, offers a completely satisfactory explanation of all the absorption results given by Buttlet and Hewitt. The absorption of both mono- and di-nitrophenols is due to the play of forces between the residual affinities of the phenol residue and the nitro-groups. The position of the absorption band depends on the absorption of the phenol residue and the number and position of the nitro-groups. When the absorption of the phenol group is shifted nearer to the red by conversion into the sodium salt, so is the spectrum of the substituted phenol also shifted in the same manner. In trinitroanisole it is evident that the single hydroxyl group is insufficient to counteract the restraining influence of the three nitro-groups. When, however, the influence of the hydroxyl is enhanced by conversion into the sodium salt, then it is sufficiently powerful to overcome the restraint of the nitro-groups, but the absorption produced is not so near the red as in the dinitrophenoxides.

It is interesting to note that with the exception of trinitroanisole, the abnormality of which is noted above, all the nitro-compounds containing the hydroxyl or amino-groups in the ortho-position with respect to the nitro-group give evidence of two bands, whilst the para-isomerides only show one absorption band. The reason for this is not clear, but it seems to be characteristic of nearly all ortho-disubstituted benzenes with two powerful groups of different type. We propose to investigate this more fully in the hopes of determining the origin.

There remains now to be described the very remarkable influence that the nature of the solvent has on the absorption of the substituted nitro-compounds. Although no definite relation has as

yet been found, all our results point to the fact that an increase in the residual affinity of the solvent causes a shift in the absorption bands towards the red. It has been known for some time that, whilst nitroquinol dimethyl ether in the solid state and in alcoholic solution is strongly yellow, the solution of this compound in light petroleum is quite colourless. We have also noticed that the same is true for α -nitronaphthalene and 4-nitro-*o*-xylene. Also we find that aqueous solutions of these compounds are even more strongly coloured than the alcoholic solutions. We have examined the absorption spectra of many of these compounds in different solvents, and find that the colour changes are simply due to shifts in the positions of the absorption bands. The solvents used were light petroleum, alcohol, water, chloroform, benzene, pyridine, and aniline. In the case of the light petroleum, Kahlbaum's best material was used (b. p. 30—50°, for the determination of fat), and it was shaken for many hours with concentrated sulphuric acid in order to remove small quantities of some unsaturated substances present, which produce a marked absorption. After this treatment the material has very slight absorption in short layers. The three last solvents have, of course, very considerable absorption, and could only be used in those cases where the absorption band of the nitro-compound is sufficiently far from the ultra-violet.

Nitroquinol dimethyl ether was examined in all the above solvents, and the position of the absorption band, as can be seen from the curves in Fig. 8, varies considerably. The position of the head of the absorption band in the various solvents is shown in the following table:

	$1/\lambda$.
Light petroleum	3000
Benzene	2900
Alcohol	2800
Chloroform	2750
Pyridine	2730
Water }	
Aniline }	2680

A maximum variation of 320 units is thus shown in the case of this substance.

Again, 4-nitro-*o*-xylene exhibits in alcohol an absorption band with head at $1/\lambda=3550$, whilst in petroleum solution the head lies at $1/\lambda=3720$ (Fig. 3).

With α -nitronaphthalene, the position of the band is as follows (Fig. 2):

	$1/\lambda$.
Light petroleum	3200
Alcohol	3100
Benzene	3050

In β -nitronaphthalene, all three bands are nearer the red in

alcoholic solution than they are in light petroleum solution, as can be seen in Fig. 2.

An analogous observation was made in the case of the three nitrotoluenes, for here it was found that a difference in the absorption occurs with the strength of the solution. As can be seen from Fig. 1 (full curves), the absorption band is most pronounced when $N/1000$ -solutions are examined. If equivalent lengths of $N/10,000$ -solutions are observed, the absorption band is less persistent (Fig. 1, dotted curves).

We would point out as a result of the observations in different solvents of the substituted nitro-compounds in which no quinonoid structure is possible, that strong presumptive evidence is obtained against the quinonoid configuration of the nitrophenols. For whereas the increase in the residual affinity of the solvent can produce a shift in the absorption bands by so great an amount where no change in configuration occurs, it is not unreasonable to argue against a radical change in configuration when an increase in the residual affinity of one of the substituent groups (OH to ONa) produces an exactly similar change, although perhaps sometimes rather greater in amount. We feel therefore that the chain of evidence against there being any radical difference between the structure of the nitrophenols and their sodium salts is completed by these observations, and therefore are bound to express ourselves against the quinonoid configuration of the nitroanilines and the sodium nitrophenoxides.

In conclusion, we wish to express our cordial thanks to Professor Crossley for his courtesy in supplying us with the nitro-derivatives of *o*-xylene, and also to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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LX.—*The Isolation of Stable Salt Hydrates, with Special Reference to the Stable Hydrates of Sodium Carbonate.*

By ALEXANDER CHARLES CUMMING.

THE actual existence of a number of salt hydrates which have been described must be regarded at present as an open question. Twelve hydrates of sodium carbonate have been described, yet Ketner (*Zeitsch.*

physikal. Chem., 1902, **39**, 645) was only able to isolate three, whilst Müller-Erzbach (*Ber.*, 1884, **17**, 1417) had decided that there were but two hydrates. This instance illustrates the need for further criteria of the existence of hydrates, since, according to the descriptions, all twelve hydrates might have been stable hydrates. New hydrates are usually isolated incidentally in the course of solubility determinations or research of a similar nature. In general, the main purpose of the experiment is not the isolation of a new or of any particular hydrate, and a brief review of these methods will show that they are not for the most part well adapted to their secondary purpose, namely, the isolation of hydrates.

Solubility Method.—The solubility curve of a substance which forms hydrates may show a break at a transition temperature. Crystallisation above this temperature will yield a lower hydrate, or the anhydrous salt, whilst crystallisation below this temperature will yield a higher hydrate. The break in the solubility curve may, however, not be obtained, as the transition temperature may be outside the range of convenient or possible measurement; thus the solubility curve for copper sulphate (Landolt-Börnstein, *Physikalisch-chemische Tabellen*, 1905, p. 537) offers no evidence of the existence of any hydrate other than the pentahydrate. Further, the solubility of a hydrate may in many cases be measured in a region where it is unstable, and this might easily lead to the non-detection of another hydrate.

The existence of a hydrate may be detected by observation of a transition point from the solubility curve or by other methods, such as the dilatometer method, but it may still remain a matter of great difficulty to isolate the indicated hydrate.

Calorimetric Method.—The existence of a hydrate may be detected from measurements of the heats of solution of the salts in various states of hydration (Thomsen, *Thermochemistry*, English translation, 1908; Donnan and Hope, *Trans. Faraday Soc.*, 1909, **5**, 244). The method is troublesome, and may not yield definite results, as, for example, Donnan and Hope have shown that this method does not reveal the existence of copper sulphate trihydrate, although it proves definitely that copper sulphate forms a monohydrate.

Vapour Pressure Method.—Another method which is not open to these objections is the measurement of vapour pressures of mixtures containing varied amounts of water. Lescoeur (*Ann. Chim. Phys.*, 1890, [vi], **21**, 511) was able to show in this way that there are only three hydrates of copper sulphate. This method is satisfactory if sufficient experiments are performed, but it is very laborious.

Desiccation with Sulphuric Acid.—If a mixture of a salt with an excess of water is placed over sulphuric acid in a closed vessel, it will be desiccated until a definite hydrate is left, provided that the aqueous

tension of the sulphuric acid employed is below that of the hydrate and greater than that of the next lower hydrate. If sufficient experiments are performed with various concentrations of sulphuric acid, it is possible to isolate all the stable hydrates of a salt. This is a practical method, and has found application in work by Ketner (*loc. cit.*) and others. Ketner states in a footnote that this method has long been used in the laboratory in Leyden.

Method under Investigation.—The method which has been investigated in this research is based on the same principle as that used in Leyden, but instead of desiccating with sulphuric acid, each hydrate was prepared by desiccation with the next lower hydrate, except in the case of the lowest hydrate, where the anhydrous salt was used as the desiccating agent.

It was shown by Andreae (*Zeitsch. physikal. Chem.*, 1897, 7, 241) that if three hydrates are placed in a closed vessel, the highest will lose water to the lowest until there are only two hydrates in the system. It may be pointed out that this is an interesting illustration of the Phase Rule. In one experiment Andreae placed a mixture of strontium chloride hexahydrate and dihydrate in one flask, a mixture of the dihydrate and anhydrous salt in another, and connected the two flasks. The first mixture lost water to the second mixture until all the hexahydrate had been converted into dihydrate, after which no further dehydration occurred. This obviously is a method for the preparation of strontium chloride dihydrate. Walker and Beveridge (*Trans.*, 1907, 91, 1797) have used this device for the preparation of *p*-toluidine monohydrate, and drew attention to the fact that a hydrate can be completely dried, without being decomposed, by the dehydrating action of the next lower hydrate, the lowest hydrate being prepared by the dehydrating action of the anhydrous substance. This should provide a method for the isolation of all the hydrates of any substance which are stable at the temperature of experiment. If a small supply of moist salt is exposed to the dehydrating action of the anhydrous salt, it should be dehydrated until the lowest hydrate is left. The total quantity of water to be taken up by the anhydrous salt must be less than sufficient to convert all of it into the lowest hydrate, so that a relatively large amount should be used. When the lowest hydrate has been isolated, it may be used to prepare the next in the series, and by continuation of the process the whole series of hydrates might be isolated. The process might also be carried out in the reverse direction, that is, the hydrates might be prepared by hydration, using the next highest hydrate in each case as the hydrating agent. Only stable hydrates have been referred to, since this method is unlikely to yield any information about hydrates unstable at the temperature of observation. Attention may be drawn also to the fact that the method

would fail if the temperature of experiment happened to be a transition temperature, since at a transition temperature it would be possible to have three hydrates in equilibrium. Up to the present the only experimental data on the subject are contained in the researches of Andreae and of Walker and Beveridge. A further examination, therefore, appeared desirable, as the results would be interesting from the point of view of the Phase Rule. In the course of the research some information was obtained as to the rate of hydration and dehydration of hydrates under various conditions, a subject about which very little is known at present.

Hydrates of Sodium Carbonate.

It was decided to apply the method to the hydrates of sodium carbonate. An exact knowledge of the hydrates of such a common substance is obviously desirable, but very conflicting statements are to be found in the literature. Two hydrates are well known articles of commerce, namely, the monohydrate and the decahydrate. Hydrates have also been described with $1\frac{1}{2}$, 2, $2\frac{1}{2}$, 3, 4, 5, 6, 7, 8, and 9 molecules of water per molecule of sodium carbonate. Another hydrate, $\text{Na}_2\text{CO}_3 \cdot 15\text{H}_2\text{O}$, has also been described, but as it was prepared only at a low temperature it may be excluded from the present discussion. All of the above hydrates from the methods of preparation and properties given by the respective authors should be stable at the ordinary temperature, but Müller-Erzbach (*loc. cit.*) could only isolate the monohydrate and decahydrate. Ketner (*loc. cit.*), by drying with various concentrations of sulphuric acid, obtained hydrates with 1, 7, and 10 molecules of water. Wells and Macadam, jun. (*J. Amer. Chem. Soc.*, 1907, 29, 721), in the course of careful solubility determinations, and Donnan and Hope (*loc. cit.*), from calorimetrical analysis, found the same three hydrates as Ketner. These recent researches leave little doubt that there are only three stable hydrates of sodium carbonate, but in view of the earlier results, further confirmation appeared desirable, especially as none of the researches provides a rigid proof of the number of stable hydrates.

EXPERIMENTAL.

Preparation of Lowest Hydrate.—The preparation of the lowest hydrate may be described in some detail, as the experiment was typical of the method adopted.

On the floor of a vacuum desiccator were placed about 100 grams of anhydrous sodium carbonate. A small weighed quantity of the decahydrate, spread in a thin layer on a watch-glass, was then introduced, and the desiccator evacuated. The apparatus was kept in

a cupboard at room temperature. From time to time the substance on the watch-glass was weighed, until no further loss in weight could be detected. The substance on the watch-glass represented the lowest hydrate, that is, the hydrate with the same vapour pressure as the mixture below, which was made up of originally anhydrous sodium carbonate plus the small amount of water obtained by dehydration of the decahydrate.

TABLE I.

Time in days.	Weight in grams.	Loss in grams.	Molecules
			H ₂ O per Na ₂ CO ₃ .
0	2.129	—	10.0
3	0.925	1.204	1.0
10	0.925	1.204	1.0
12	0.925	1.204	1.0

The substance lost water until Na₂CO₃.H₂O was left, after which no further dehydration was detected. In all the later experiments the substance was roughly ground at the start of an experiment. When the weight had become constant, it was ground to a fine powder, and the experiment continued. In no case was a further change in weight noticed with hydrates of sodium carbonate. The composition was calculated from the weight of water lost, and, as a check, the hydrate obtained was analysed, except in the first experiment, where this was not done.

Hydrate next above the Monohydrate.—An intimate mixture of anhydrous and decahydrated sodium carbonate was made in the proportion calculated to give the monohydrate, and the mixture was kept in an evacuated vessel for three weeks before use. A small weighed quantity of sodium carbonate was then dehydrated by a large amount of this mixture.

TABLE II.

Time in days.	Weight in grams.	Loss in grams.	Molecules
			H ₂ O per Na ₂ CO ₃ .
0	2.391	—	10.0
1	2.206	0.185	8.8
2	2.079	0.312	7.9
7	1.942	0.449	7.02
13	1.941	0.450	7.01
16	1.941	0.450	7.01

In this experiment the dehydrating agent was a mixture of anhydrous and decahydrated sodium carbonates in the proportion calculated to yield the monohydrate. As there was a remote possibility that the monohydrate had not been formed, it was prepared in another way. The crystalline decahydrate was melted on the steam-bath and evaporated until a sufficient quantity of the monohydrate had separated. This was filtered from the hot solution. Analysis showed these crystals to have the empirical composition Na₂CO₃.1.2H₂O, that is, they were crystals of the monohydrate mixed

with a small proportion of a higher hydrate. A small weighed sample of the decahydrate was then dehydrated by 100 grams of this monohydrate.

TABLE III.

Time in days.	Weight in grams.	Loss in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
0	2.438	—	10.0
5	2.158	0.280	8.0
11	1.981	0.457	7.2
14	1.976	0.462	7.0
21	1.976	0.462	7.0

The substance was then finely ground. No further loss was detected after seventy-three days in an evacuated vessel.

Hydrate next above the Heptahydrate.—It was found that no dehydration of the decahydrate had taken place after seven days in an evacuated vessel above a mixture of hydrates which had the empirical composition $\text{Na}_2\text{CO}_3 \cdot 7.3\text{H}_2\text{O}$. There is no evidence, therefore, of any hydrate intermediate between the heptahydrate and decahydrate.

Hydration of a less Hydrated Salt.

In the previous experiments a hydrate was dehydrated by a lower hydrate until the hydrate next in the series to the lower hydrate was obtained. The process may be carried out in the reverse manner, that is, a substance may be hydrated by a higher hydrate until the hydrate next below the higher hydrate is formed.

Hydrate next below the Decahydrate.—A small weighed sample of the anhydrous salt was hydrated by a large supply of slightly effloresced decahydrate.

TABLE IV.

Time in days.	Weight in grams.	Increase in grams.	Molecules H ₂ O per Na ₂ CO ₃ .
—	1.717	—	—
1	2.123	0.406	1.4
4	2.328	0.611	2.1
11	2.673	0.956	3.3
15	2.777	1.060	3.6
19	2.900	1.183	4.1
25	3.238	1.521	5.2
28	3.305	1.588	5.5
39	3.540	1.823	6.3
50	3.722	2.005	6.9
96	3.738	2.021	6.93
216	3.738	2.021	6.93

The amount of water given in the last column is calculated from the gain in weight, on the assumption that the sample was quite anhydrous at the beginning of the experiment, but a trace of water must have been present, as analysis showed that the substance finally obtained was pure $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$.

It will be noticed that the first molecule of water was taken up very quickly, and the remainder at a much slower rate. This experiment taken alone indicates the probable existence of a monohydrate.

The existence of $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ was indicated in a similar manner during the dehydration of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ by anhydrous magnesium sulphate. One-seventh of the water was lost in the first day, and the dehydration then became extremely slow.

Hydrate next below the Heptahydrate.—A small weighed sample of anhydrous salt was hydrated with 100 grams of the heptahydrate.

TABLE V.

Time in days.	Weight in grams.	Increase in grams.	Molecules H_2O per Na_2CO_3 .
0	0.607	—	—
2	0.608	0.078	0.76
22	0.709	0.102	0.99
36	0.712	0.105	1.02
58	0.712	0.105	1.02

Highest Hydrate of Sodium Carbonate.—A small weighed quantity of anhydrous sodium carbonate was exposed to the hydrating action of a saturated solution with which was mixed a large supply of crystals.

TABLE VI.

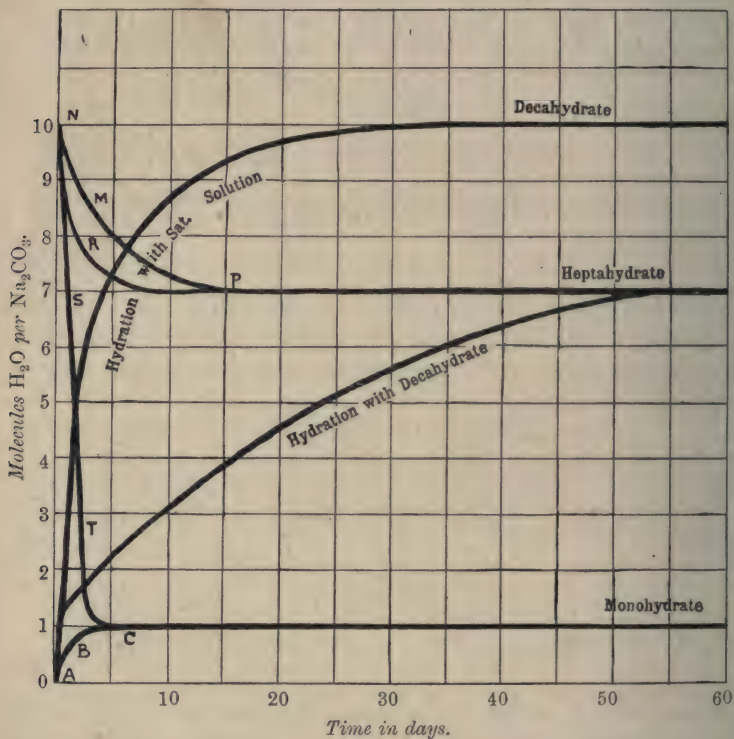
Time in days.	Weight in grams.	Increase in grams.	Molecules H_2O per Na_2CO_3 .
—	0.735	—	—
1	1.210	0.585	4.7
2	1.379	0.644	5.2
3	1.566	0.881	6.7
4	1.633	0.896	7.2
7	1.753	1.018	8.1
11	1.853	1.118	9.0
37	1.985	1.250	10.01
51	1.985	1.250	10.01

The results in these tables have been expressed graphically in the diagram. The experiments were carried out at room temperature, and the mean temperature would be about 12° .

It is evident that with these hydrates, dehydration of a small quantity of substance provides a quicker process for the preparation of a hydrate than does the hydration method.

The two curves showing dehydration to the heptahydrate illustrate the difference in time produced by a slight variation in the conditions of the experiment. A first inspection of these results would suggest that a rigid proof has been obtained that there are three, and not more than three, stable hydrates of sodium carbonate. The existence of the three hydrates with 1, 7, and 10 molecules of water is certainly proved, but consideration will show that the existence of

other hydrates is possible, although very improbable. There is no proof, and at present no rigid proof is possible, that a hydrate has not been completely passed over during hydration and dehydration. From the nature of the experiments this is very improbable, but it is at least theoretically possible, and the phenomena now to be recorded will prove that non-formation of an intermediate hydrate is at least a possibility.



The hydration curves start in each case from anhydrous salt, and the dehydration curves start in each case from sodium carbonate decahydrate.

Curve A B C shows hydration with heptahydrate (Table V).

Curves N M P and N R P show dehydration with monohydrate (Tables III and II).

Curve N S T C shows dehydration with anhydrous salt (Table I).

Non-formation of a Hydrate.—In the experiment recorded on the hydration with saturated solution to obtain the decahydrate, the following phenomena were noticed. The anhydrous salt was spread in a thin layer on the surface of a watch-glass. After one day it was found that some small detached portions of the salt had deliquesced

with the formation of small drops of solution on the glass. Some of these were touched with the end of a fine platinum wire which had been drawn across the surface of a crystal of sodium carbonate decahydrate. Each drop as it was touched crystallised instantly and completely, which proved that a supersaturated solution had been formed instead of the expected solid decahydrate phase. In the course of the first few days all the drops crystallised, with the exception of two minute drops. These were still present at the end of thirty-seven days, and when these were touched they did not crystallise completely. The formation of the drops of supersaturated solution at the beginning of the experiment is mainly remarkable in that there cannot have been any nucleus present to start the formation of decahydrate, despite the fact that the floor of the vessel was covered with moist crystals of the decahydrate. The supersaturated solution would have a lower vapour pressure than the wet decahydrate system, and would therefore continue to absorb water. In absence of a nucleus of decahydrate, the absorption of water would continue, it is to be supposed, until these drops had the same vapour pressure as the system below, that is, until a "saturated solution" had been formed. This agrees with the fact that only partial crystallisation occurred when the drops were artificially seeded, since the liquid left after the crystallisation must have been "saturated solution." If this explanation be accepted, "saturated solution" was formed without formation of the intermediate phase, the decahydrate. The experiment has been repeated three times, and in two cases the solution phase was formed. In all cases most of the salt hydrated directly to the solid hydrate, but small detached drops of solution formed in places on the glass.

Method for the Isolation of a new Hydrate.—From the results obtained with sodium carbonate it might seem that the method outlined in the earlier part of this paper would quickly lead to the isolation of all the hydrates of any salt. From experiments with other salts, however, it appears that sodium carbonate is a particularly favourable case, and a considerable search may be necessary before another salt is found which yields a series of hydrates so quickly and completely at the ordinary temperature. Magnesium sulphate heptahydrate, dehydrated by anhydrous magnesium sulphate, lost one seventh of its water in the first twenty-four hours, and then lost water, steadily but very slowly. At the end of one hundred and forty-five days the additional amount of water lost corresponded with a loss of only half a molecule of water, and there was no appreciable increase in the rate of dehydration after fine grinding. With several other salts it was found that hydration or dehydration may occur with extreme slowness. From the experience gained in this research, I am of opinion that the systematic search for all the hydrates of a salt

would in most cases prove too tedious and troublesome to repay the labour. At the same time it appears probable that the existence or otherwise of any particular hydrate may be readily determined by means of this method. The method has the further important practical advantage that if the hydrate has any existence it will be obtained in a pure state. If the existence of a hydrate with n molecules of water is suspected, two experiments should be performed.

On the floor of a desiccator place a quantity of an artificial finely powdered mixture which contains a little less than n molecules of water per molecule of anhydrous salt. On a watch-glass above it place a little finely powdered mixture, with a little more than n molecules of water, and exhaust the vessel. The substance on the glass will lose water until the pure hydrate is left, if there is a stable hydrate of that composition. This was the method used by Walker and Beveridge for the preparation of *p*-toluidine monohydrate. I would suggest that a second experiment should be performed, using a large quantity of a mixture containing slightly more than n molecules of water to hydrate a small quantity of a mixture with slightly less than n molecules of water. In all cases it is expedient to evacuate as thoroughly as possible. The method would probably be of value in organic chemistry for the preparation in a pure state of substances which readily dissociate into their constituents, such as iodine additive compounds and alcohol additive compounds corresponding with hydrates (alcoholates).

Suspended Transformation.—A curious case of suspended transformation was noticed in some experiments with the hydrates of copper sulphate. The dehydrating agent was a large supply of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$ in the form of a fine powder mixed with a small proportion of powdered pentahydrate. A small weighed quantity of the pentahydrate was to be dehydrated. The pentahydrate had been recrystallised, and was ground to a coarse powder before a sample was taken. It was found that 2.282 grams had lost in two days only 0.004 gram of water, and the colour of the crystals was unchanged. After three more days the weight was unchanged. The crystals were then touched with a platinum spatula, which had been dipped in the mixture below. No weighable quantity had been added, but a nucleus of a lower hydrate had evidently been introduced, as efflorescence started in two places and spread through the whole mass.

TABLE VII.

Time in days.	Weight in grams.	Loss in grams.	Molecules H ₂ O per CuSO ₄ .
0	2.282	—	5.0
2	2.278	0.004	—
5	2.278	0.004	—
12	1.928	0.354	3.69
33	1.914	0.368	3.62
145	1.847	0.435	3.37
175	1.839	0.443	3.35
182	1.830	0.452	3.31
212	1.795	0.487	3.18

From this table it will be seen that once the action had started, dehydration proceeded steadily, but so slowly that it had not attained completion in seven months. The suspended transformation in this experiment is interesting, in that the vapour pressure in the apparatus was fixed by the presence of a mixture of monohydrate with a little trihydrate on the floor of the vessel. The initial small loss probably indicates a trace of surface moisture, and it is possible that on this account the grinding did not start the formation of a lower hydrate.

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LXI.—*Affinity Relations of Cupric Oxide and of Cupric Hydroxide.*

By ARTHUR JOHN ALLMAND.

IN the course of a recent paper (Trans., 1909, 95, 2151), the author showed that crystalline cupric hydroxide when treated with concentrated alkali solutions at the ordinary temperature, or when shaken with dilute aqueous ammonia at 25°, loses its water and is converted into cupric oxide. According to these facts, crystalline cupric hydroxide is unstable with respect to cupric oxide and the given aqueous solution at the temperatures in question, whereas the reverse has been thought to be the case. To decide this point tensimetric and electrometric experiments were undertaken. If in reality crystalline cupric hydroxide constitutes an unstable system at the ordinary temperature, it must have a higher vapour pressure than water, or the alkaline and ammoniacal solutions referred to, and yet it appears to be perfectly stable in dry air. Secondly, it must also be more soluble than cupric oxide, and the system $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{alkali}$ should give

a lower single potential difference value than the system $\text{Pt} \left| \begin{array}{l} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right|$ alkali, although it is not certain a priori that the solubility difference will be sufficiently great to be detected.

Tensimetric Experiments.

A tensimeter was filled with all the ordinary precautions. One bulb contained a sample of "Becquerel" cupric hydroxide (*Compt. rend.*, 1852, **34**, 573), which had been dried at 100° , bottled, and subsequently left in a dessicator over calcium chloride. The other bulb contained phosphoric oxide, and the indicating liquid in the U-tube was olive oil. The tensimeter was placed in a thermostat at 25° . Readings were taken over some four months, at the end of which time the cupric hydroxide had undergone no marked change in colour. The following table contains the results.

TABLE I. Temperature 25° .

Time of observation.	Reading in mm. of olive oil.
September 27	Filled and sealed: kept limbs in connexion.
" 28	Allowed oil to flow into U-tube; placed in thermostat.
" 29	7
" 30	8
October 2	9—10
" 4	9—10
" 6	9—10
" 20	13—14
November 2	13—14. Took out, and allowed limbs to stand in connexion 15 hours. Replaced. Reading rose very slowly.
" 15	3—4
" 29	3—4. Put limbs once more in connexion for 3 hours. Replaced.
December 1	3—4
" 7	2—3
" 9	2—3
" 11	2
" 15	<2
" 21	<2
January 5	1·5. Put limbs into connexion once more for 24 hours. Replaced.
" 20	1·5

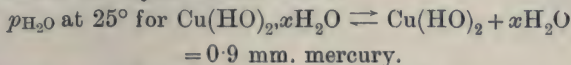
The vapour pressure of water at 25° is about 23·5 mm. of *mercury*, whilst the highest pressure observed in the tensimeter was about 13·5 mm. of *olive oil*. This supported the view that cupric hydroxide is the stable system. It was, however, possible that the dehydration did not commence, owing to powerful opposing reaction resistances, and that by the addition of some quantity of a decomposition product these reaction resistances could be overcome. A second tensimeter was therefore filled, containing in one limb a mixture of cupric

hydroxide together with cupric oxide, prepared by the action of aqueous ammonia at 25° on cupric hydroxide. The measurements obtained are given in the following table :

TABLE II. Temperature 25°.

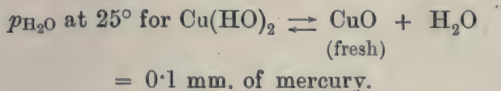
Time of observation.		Reading in mm. of olive oil.
December	2	Started
"	7	9
"	9	9·5
"	11	11·5
"	15	11·5
"	21	12·5
January	5	13·5. Placed limbs in connexion for 24 hours.
"	20	Replaced. 1·5

It will be seen that the figures are practically identical with those in table I, furnishing further evidence in favour of the view that crystalline cupric hydroxide is stable with respect to copper oxide and water. The fact that the same two final figures—13·5 mm. and 1·5 mm.—occur in both tables points to their corresponding with two definite equilibrium states. It has been already shown (*loc. cit.*) that crystalline cupric hydroxide contains more water (in the ratio 1·07 : 1) than is demanded by the formula $\text{Cu}(\text{HO})_2$, and that it is improbable that this excess is physically held or adsorbed. It was suggested that the excess may be due to the presence of small quantities of a higher hydrate, such as $\text{CuO} \cdot 2\text{H}_2\text{O}$. If that view be taken, we can perhaps ascribe the higher of the two vapour pressures observed to the presence of this hydrate, and write :



(The specific gravity of olive oil is taken as 0·9.)

In any case it is highly probable that the lower vapour pressure measured corresponds with the dehydration of cupric hydroxide to copper oxide and water, and we can write :



Electrometric Measurements.

The electrode measured was always of the type $\text{Pt} \left| \begin{array}{l} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{alkali.}$

With the exception of a few experiments carried out with *N*-potassium hydroxide and *N*/10-sodium hydroxide, the electrolyte employed was *N*-sodium hydroxide (carbonate-free). The electrode vessels were adapted for shaking and similar to those already described (*loc. cit.*), whilst the measuring apparatus—galvanometer, Weston element,

metre bridge—calls for no remark. The electrodes were gently revolved on a wheel, shaken, and taken off and measured against calomel electrodes at various intervals for some length of time. All readings were made at the ordinary temperature, namely, 17° . The potential of the *N*-calomel electrode was taken as $+0.282$ volt at 17° , the liquid potential difference between *N*-potassium chloride and *N*-sodium hydroxide as 0.020 volt.

In the first experiments, cupric oxide was used, prepared by thorough ignition of cupric hydroxide or cuprous oxide over a Bunsen burner. Now the single potential difference given by the system $\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right. \text{N-NaOH}$ is -0.074 volt (*loc. cit.*), and judging from the results of the vapour-pressure measurements, the combination $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{N-NaOH}$ should give a more positive value, corresponding with a tendency for the change $\text{CuO} + \text{H}_2\text{O} \rightarrow \text{Cu}(\text{HO})_2$ to take place. As a matter of fact, the behaviour of the electrodes was as follows. They commenced (read the day after setting up) by giving considerably more negative values than the cupric hydroxide electrode, and then slowly fell, becoming more and more negative, and in some cases finally reaching or approaching an asymptotic value. For example, an electrode set up containing *N*-sodium hydroxide and cupric oxide, prepared by igniting cuprous oxide, gave the following readings.

TABLE III. Temperature 17° .

Days after setting up.	Single potential $\text{Pt} \left \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{N-NaOH}$.
1	-0.096 volt
3	-0.109 „
4	-0.112 „
5	-0.114 to -0.115 volt
6	-0.117 „
7	-0.118 „
8	-0.119 „
10	-0.120 „
11	-0.120 to -0.119 „
12	-0.120 to -0.119 „
14	-0.121 to -0.122 „

The rate of fall of potential was very different in different cases, as was also its extent. The first explanation which suggests itself is that the electrode is not acting reversibly. Of electrode systems in which the reaction taking place is not the complete discharge of an ion to a neutral substance, but only an increase or decrease in the number of ionic charges, it is known that but few behave reversibly, and this is particularly the case in alkaline solutions. On the other hand, the particular reaction $\text{Cu}^{++} \rightleftharpoons \text{Cu}^+ + \oplus$ is reversible in acid solution,

and there is every reason from the behaviour of the $\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right.$ alkali electrode to assume that it is also reversible in alkaline solution. Luther (*Zeitsch. Elektrochem.*, 1907, 13, 289) has declared the criteria of irreversibility of an electrode to be (amongst others): (1) fluctuations in potential value; (2) two electrodes in the same solution giving different values; (3) changes on shaking, and (4) changes in concentration of the electrolyte not bringing about the corresponding theoretical potential changes.

In the present case, the variation in potential was always a directed one—a fall. To test the second point an electrode vessel was made up containing two electrodes (one blank and one platinised) about 2 cm. apart, dipping into the same mixture of depolariser and electrolyte. They were measured over a period of five weeks, during which time the potential fell by 0.025 volt, and they always agreed to within 0.0004 volt. It was further found that shaking never altered the potential of any electrode by more than a millivolt, and the original value was restored within a minute or two on standing.

$\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right.$ alkali electrodes gave the theoretical change on altering the concentration of the alkali (slight deviations could be otherwise explained), and a few experiments carried out with $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right.$ alkali electrodes, using alkali of different concentrations, gave indication of the same behaviour. That cupric hydroxide is really far more soluble than cupric oxide is also shown by the fact that, whereas the former when shaken up with alkali and an excess of finely-divided copper is completely converted into cuprous oxide within a few days, cupric oxide was found to be only altered slightly by a month's shaking. It seems justifiable to assume therefore that the electrode is acting reversibly, and giving the true potential corresponding with the relative concentrations in the solution at any moment of Cu^{++} and Cu^+ ions.

This being so, the only other explanation open is that some kind of change is taking place in the copper oxide, rendering it less soluble. This view seems particularly plausible, as cupric oxide is not crystalline but amorphous, and as such is subject to the phenomenon of *ageing*, which is bound up with a progressive decrease in solubility. The nature of this process is still obscure. It has been regarded as the result of a slow crystallisation taking place in the amorphous mass, looking on the latter as a supercooled liquid. This does not seem very probable, as the solubility of the material should not then appreciably alter until completely changed into crystalline substance. The phenomenon is particularly well marked in the cases of precipitated colloidal substances (*Zeitsch. anorg. Chem.*, 1899, 20, 185; 1900, 25,

155; 1901, 27, 390; 1901, 28, 474; 1902, 30, 331; 1904, 38, 377; 1904, 40, 428; 1905, 46, 333, etc.). It is there accompanied by a probable loss of water, and by a striking decrease in the bulk and surface of the precipitate, and Hantzsch (*Zeitsch. anorg. Chem.*, 1902, 30, 338) has ascribed the lowering in solubility to both chemical and physical reasons, the former depending on the supposed molecular dehydration which accompanies the ageing, and the latter being due to the great decrease in surface which is the result of the spontaneous coagulation of the material. Ostwald (*Zeitsch. physikal. Chem.*, 1900, 34, 395) had previously advanced the conception of dependence of solubility on surface or size of grain to account for the differences displayed between the red and yellow forms of mercuric oxide, and the idea was further extended to other substances (all crystalline) by Hulett (*Zeitsch. physikal. Chem.*, 1901, 37, 385), Hulett and Allen (*J. Amer. Chem. Soc.*, 1902, 24, 667), and von Steinwehr (*Zeitsch. Elektrochem.*, 1906, 12, 578). It has been lately shown (Trans., 1909, 95, 2151, and unpublished work of the author) that the initial decrease observed in the single potential readings of the system $\text{Pt} \left| \begin{array}{l} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right. \text{alkali}$ and $\text{Hg} \mid \text{HgO alkali}$ can be ascribed to a spontaneous diminution in solubility due to the same cause.

In the present case the author is disinclined to adopt that explanation. As will be seen, the difference between the highest and lowest values experimentally obtained with the $\text{Pt} \left| \begin{array}{l} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right. \text{alkali electrodes}$ is 0.093 volt, which corresponds with a ratio of solubilities in the two cases of about 40:1. On the other hand, the greatest ratio in which the solubility of a substance has been increased by alteration of the surface conditions is 3:1 (Hulett, *loc. cit.*). Further, the colloidal hydroxides to which Hantzsch has applied Ostwald's conception do certainly show a very remarkable diminution of surface when ageing, whilst the samples of copper oxide with which the author has worked undergo no such change.

A more probable explanation is that the phenomenon is due to gradual polymerisation of the molecules of the copper oxide, and that at any moment between the time of preparation of the fresh substance and the time of complete ageing we have a solid solution containing two (or more) kinds of molecules of different complexity in proportions which do not correspond with the equilibrium ratios. Assuming, then, that the more complex molecule is the less soluble, and that the freshly prepared material has an undue preponderance of simple molecules, the solubility of a sample of copper oxide will slowly fall, until a value has been reached corresponding with the equilibrium concentrations of the different kinds of molecules. When shaken up with something

which can exert a solvent action, the velocity of the process will be increased. Alkali solutions must have that effect, owing to the slight amphoteric nature of the copper oxide; and it is found by experience that left to itself, the oxide alters very slowly indeed, but that it ages in contact with alkali, and more rapidly in a concentrated than in a dilute alkaline solution. We will adopt this polymerisation conception as a working hypothesis. Then it is very probable that the equilibrium of the different kinds of molecules will shift with increase of temperature, and in favour of the less associated molecule, the formation of which is probably accompanied by absorption of heat. Further, the rate at which equilibrium is reached will be greater the higher the temperature; and consequently, until equilibrium has set in, determinations of solubility, potential difference, dissociation pressure, etc. (all of them related quantities) will yield results depending to a greater or less extent on:

- (a) Temperature of preparation of sample.
- (b) Time during which it was kept at that temperature.
- (c) Rate of passage from temperature of preparation to temperature of measurement.

And the influence of the temperature of measurement will be a two-fold one, due to:

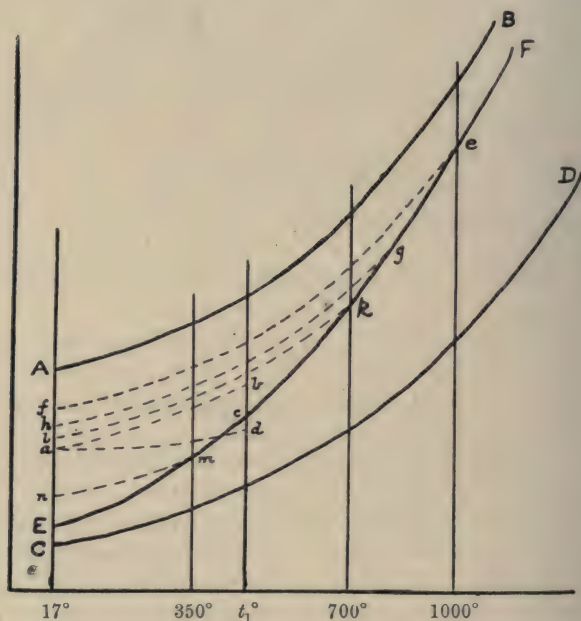
- (a) The change of solubility, etc., of each different kind of molecule with change of temperature, and
- (b) The variation in the relative proportions of the different kinds of molecules with change of temperature.

In Fig. 1, temperature is plotted along the abscissa and along the ordinate solubility or dissociation pressure of the oxide. *AB* would represent the curve supposing all the molecules to be simple, and *CD* supposing them all to be complex, whilst *EF* is the actual equilibrium curve, which moves nearer to *AB* as the temperature rises, corresponding with a decrease in the proportion of the more complex molecules.

With the simple assumptions already made, it is possible to trace qualitatively on the above curve the behaviour of any sample of copper oxide on heating or cooling or measurement. Let, for example, the line *AEC* correspond with 17° , at which temperature a specimen of copper oxide is made by withdrawing water from cupric hydroxide. It will initially have the dissociation pressure corresponding with *A*. This will fall pretty rapidly at first along the line *AE*. Suppose when the point *a* is reached the oxide be heated to a temperature t_1° . If no further polymerisation were to take place, its path would be along the line *ab*. Polymerisation will continue, however, and the more rapidly the higher the temperature (although the closer proximity of the curves *ab* and *Ec* at the higher temperature will tend to diminish the rate of change). The actual path followed then will fall

below ab , but close to it if the temperature be raised rapidly. If the temperature be raised *very* slowly, then the equilibrium curve Ec will be reached proportionately sooner, and followed until c is reached. At intermediate or variable rates of increase of temperature, the line bc may finally be struck, or the curve Ec cut, and a point below it, such as d , ultimately reached. Hence, at the temperature t_1° the initial dissociation pressure given by the oxide may be equal to, greater than, or less than the equilibrium value.

FIG. 1.



We will now attempt to interpret the single potential readings which were obtained for the system $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH}$ in terms of the conception developed above.

1. *Value of Point A* (Fig. 1).—This is not given directly by electrometric measurements, but can be deduced from the tensimeter readings already discussed.

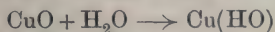
We have :

$$p_{\text{H}_2\text{O}} \text{ at } 25^\circ \text{ for } \text{Cu}(\text{HO})_2 \rightleftharpoons \text{CuO} + \text{H}_2\text{O} \\ = 0.1 \text{ mm. mercury,}$$

and

$$p_{\text{H}_2\text{O}} \text{ at } 25^\circ \text{ for pure water} \\ = 23.5 \text{ mm. mercury.}$$

Hence the decrease in free energy of the reaction



(freshly
prepared)

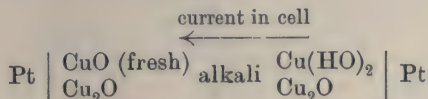
at 25° is $RT \ln \frac{23.5}{0.1}$

$$= 0.06 \log. 235 \text{ volt-faradays}$$

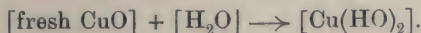
$$= 0.06 \times 2.37 \text{ volt-faradays.}$$

It will not be very different at 17° .

If the cell



were to be set up, the chemical result for the passage of *one* faraday would be the same reaction, namely :



$$\text{Hence } E.M.F. = 0.06 \times 2.37 \text{ volts}$$

$$= 0.142 \text{ volt.}$$

$$\text{We know that Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH} = -0.074 \text{ volt}$$

Therefore,

$$\text{Pt} \left| \begin{array}{c} \text{fresh CuO} \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH} \\ = +0.068 \text{ volt.}$$

2. *Value of Point E* (Fig. 1).—For this value the author has taken the lowest figure reached in any of the measurements, that is, -0.154 volt. It was obtained with a sample of cupric oxide prepared by ignition of cupric nitrate. As the accompanying figure (2) shows, it was approached asymptotically, which fact supports the view that it represented the true equilibrium value. The other curve on the same diagram was given by a sample of oxide obtained by ignition of cuprous oxide. Although not followed to the end (the electrode vessel broke), it appears likely that it would have reached the same limiting value. As we shall see later, there is another reason for thinking that -0.154 volt is very near the correct value.

3. *Samples of Oxide aged at 950 — 1000° .*—Some cupric oxide (i), prepared by igniting crystalline cupric hydroxide, was placed in a platinum crucible and heated in a platinum-wound electric heater

at 800 — 900° for 3 hours.

„ 900 — 950 „ 1 hour.

„ 950 — 1000 „ 3 hours.

„ 1000° „ 1 hour.

A second sample (ii), also from cupric hydroxide, was similarly heated

at 800—900° for 1½ hours.

„ 900—950 „ 2½ „

„ 950—970 „ 8 „

In both cases the oxide was allowed to cool in the furnace after shutting off the current. The following readings resulted, using electrodes containing the above oxides.

FIG. 2.

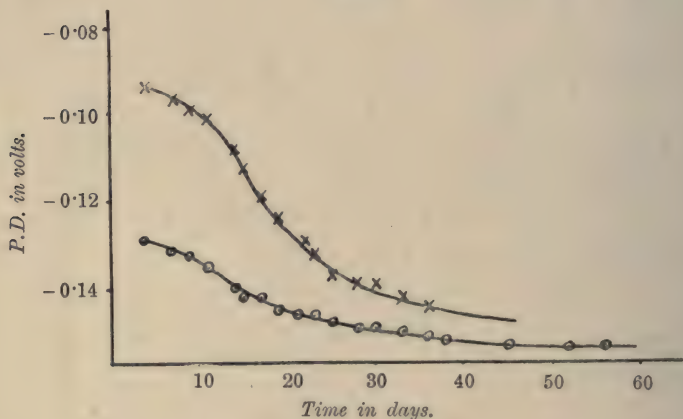


TABLE IV. Temperature 17°.

Time after setting up.	Potential Pt $\left \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right N\text{-NaOH in volts.}$	
	(i)	(ii)
1 day	-0.061 volt	—
2 days	—	-0.063 volt
5 „	-0.064 „	—
9 „	-0.067 „	—
13 „	—	-0.073 „
20½ „	-0.076 „	—
22 „	—	-0.078 „
29 „	—	-0.081 „
36 „	—	-0.084 „

Referring to Fig. 1, it is seen that for a high temperature, such as 1000°, at which equilibrium will be quickly reached, and at which the proportion of simple molecules is comparatively high, the copper oxide dissociation pressure will correspond with a point such as *e*. If suddenly chilled, the ratio of the different molecular species would remain unaltered, and the falling dissociation pressure would follow the line *ef*. When measured electrometrically at room temperature, a very high initial value would result. If cooled more slowly, as was

actually the case, the curve EF would probably be followed for some time and then gradually left, the path egh being taken. The point, h , finally reached would correspond with the initial potential value, -0.061 volt, given by these oxide samples. It is interesting to notice that these samples of oxide when first measured were unstable with respect to cupric hydroxide, the potential $\text{Pt} \left| \begin{array}{c} \text{Cu}(\text{HO})_2 \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH}$ being -0.073 volt.

4. *Samples of oxide prepared by ignition of cupric nitrate, cupric hydroxide, or cuprous oxide in an open porcelain crucible over a Bunsen flame.*—The results of some of the preparations are shown in table III and in Fig. 2. Other figures were as follows :

TABLE V. Temperature 17° .

Time in days after setting up.	Single Potential Pt $\left \begin{array}{c} \text{Cu}_2\text{O} \\ \text{CuO} \end{array} \right. N\text{-NaOH}$ in volts.			
	a.	b.	c.	d.
1	-0.103	-0.107	$\left. \begin{array}{l} -0.107 \\ -0.110 \end{array} \right\}$	-0.097
2	-0.118	$\left. \begin{array}{l} -0.109 \\ -0.112 \end{array} \right\}$	—	—
3	-0.123	-0.114	$\left. \begin{array}{l} -0.114 \\ -0.115 \end{array} \right\}$	—
4	-0.125	-0.115	—	—
14	—	—	—	-0.106
23	—	—	—	-0.113
30	—	—	—	-0.115
37	—	—	—	-0.118

These preparations were never subjected to such a high temperature as those discussed under (3), and they were also cooled far more rapidly. During this process one would expect them to follow nearly the line kl , falling a little below it only. The value l corresponds with the initial figure of -0.097 to -0.107 volt given in the table. The differences observed will be the result, amongst other things, of differences in time of heating, rate of cooling, etc.

5. *Samples of Oxide aged at 350° .*—Two samples of crystalline cupric hydroxide contained in porcelain crucibles were heated in a nickel-wound electric heater to $330\text{--}350^\circ$ for twenty hours. The crucibles were then taken out and allowed to cool. Two electrodes were made up and measured in the ordinary way. They gave :

(a) -0.135 (2nd day); -0.134 (13th day).

(b) -0.133 (3rd day); -0.133 (10th day); -0.135 (17th day).

There was thus hardly any alteration during the time of measurement, and, moreover, the two sets of figures agree very well with one another. From this fact we conclude that equilibrium was probably reached in the two cases, and frozen by the rapid cooling,

during which the dissociation pressure would follow the line *mn*. Thus, a low initial value would result.

6. *Samples of Oxide prepared at low temperatures.*—Oxide was prepared by dehydrating cupric hydroxide with aqueous ammonia at 25° and with aqueous potassium hydroxide at 70°. The potential values of electrode systems containing preparations of oxides thus made only fell very slowly; although in one case measured for five weeks, values lower than -0.117 volt were never reached, as the table shows:

TABLE VI. Temperature 17°.

Time in days after setting up.	Potential difference Pt $\left \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right.$ N-NaOH in volts.						
	1.	2.	3.	4.	5.	6.	7.
1	—	-0.106 } -0.109 }	-0.108 } -0.109 }	—	-0.099 } -0.100 }	-0.011	-0.102
2	-0.106 } -0.109 }	-0.113 } -0.114 }	—	—	-0.100	—	—
3	-0.114	—	—	—	-0.102	—	—
4	-0.115	-0.116	—	-0.111	—	-0.113	-0.108
5	—	—	—	—	-0.105	-0.114	—
6	—	—	—	—	—	—	-0.111
7	—	—	—	-0.111	—	-0.113	—
8	—	—	—	—	-0.105	—	—
9	—	—	—	-0.113	—	-0.116	-0.111
10	—	—	—	—	-0.105	—	—
11	—	—	—	-0.114	—	-0.115	—
12	—	—	—	—	—	—	-0.114
13	—	—	—	—	-0.107	—	—
14	—	—	—	-0.114	—	—	-0.116
16	—	—	—	—	-0.107	—	—
18	—	—	—	—	-0.108	—	—
19	—	—	—	-0.113	—	—	—
25	—	—	—	—	-0.111	—	—
28	—	—	—	—	—	—	-0.116
32	—	—	—	—	-0.113	—	—
35	—	—	—	—	-0.112	—	—

It is evident that reference to Fig. 1 can interpret satisfactorily the initial values given by the different electrodes, but gives no explanation of the reason for the very different rates of ageing at 17° of samples of copper oxide which have been heated to different temperatures. It has been seen that oxide which has been heated to 1000° alters slowly and regularly, that oxides which have been prepared at temperatures of 700—800° age at varying speeds, and that oxides heated only to 350° or below alter very slowly indeed. It is probable that these differences are due to variations in the nature of the surface of the material or to similar causes, but more it is impossible to say. Apart from this point, if the view developed here that the changes observed during ageing are the result of polymerisation be accepted as correct, it is obvious that electromotive measurements may prove to be

a very valuable method for the investigation of the molecular complexity of certain solid substances.

It should be mentioned here that Immerwahr (*Zeitsch. Elektrochem.*, 1900-1, **7**, 477), Johnson (*Trans. Amer. Electrochem. Soc.*, 1902, **1**, 187), and Lorenz and Hauser (*Zeitsch. anorg. Chem.*, 1906, **51**, 81) have all worked on electrodes of the type $\text{Cu} \mid \text{CuO}$ alkali, which, however, have been shown by the author to be unstable, owing to cuprous oxide formation. It is interesting to note that Immerwahr found that oxide prepared from copper nitrate gave much more negative values than oxide prepared by precipitation from hot aqueous solution by alkali.

Calculations of Affinity Values.

We are now in a position to understand the relationships to one another of cupric hydroxide and cupric oxide. We have the following three potential differences at 17° :

$$\text{Pt} \mid \begin{array}{l} \text{fresh CuO} \\ \text{Cu}_2\text{O} \end{array} \quad N\text{-NaOH} = +0.068 \text{ volt.}$$

(Calculated approximate
probable value)

$$\text{Pt} \mid \begin{array}{l} \text{Cu}(\text{HO})_2(\text{crystalline}) \\ \text{Cu}_2\text{O} \end{array} \quad N\text{-NaOH} = -0.074 \text{ volt.}$$

$$\text{Pt} \mid \begin{array}{l} \text{stabilised CuO} \\ \text{Cu}_2\text{O} \end{array} \quad N\text{-NaOH} = -0.154 \text{ volt.}$$

The change $[\text{Cu}(\text{HO})_2] \rightarrow [\text{CuO}] + [\text{H}_2\text{O}]$.
(Crystalline) (Fresh) (Liquid)

$$\begin{aligned} \text{absorbs} \quad & 96540 \times [0.068 - (-0.074)] \text{ joules} \\ & = 96540 \times 0.142 \\ & = 13700 \text{ joules.} \end{aligned}$$

The change $[\text{Cu}(\text{HO})_2] \rightarrow [\text{CuO}] + [\text{H}_2\text{O}]$.
(Crystalline) (Stabilised) (Liquid)

$$\begin{aligned} \text{gives out} \quad & 96540 \times [-0.074 - (-0.154)] \text{ joules.} \\ & = 96540 \times 0.08 \\ & = 7720 \text{ joules.} \end{aligned}$$

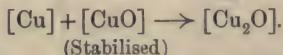
If, however, the stabilised copper oxide is prepared directly from the cupric hydroxide, fresh solid cupric oxide, not an aqueous solution, being the intermediate stage, we are dealing with two successive reactions: (a) reversible formation of fresh $[\text{CuO}]$, absorbing 13700 joules, and (b) irreversible formation of stabilised $[\text{CuO}]$, giving out 21420 joules; and dehydration cannot set in except when the aqueous vapour pressure of the system is kept below 0.1 mm. Then it will take place very slowly, its rate being determined by that of the reaction:



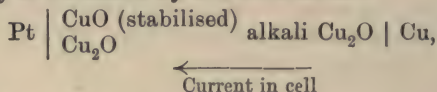
When, however, the change $\text{Cu}(\text{HO})_2 \rightarrow \text{CuO (stabilised)} + \text{H}_2\text{O}$ has

an opportunity of taking place without the intermediate formation of "fresh" cupric oxide, it will set in. This will happen, for example, if the cupric hydroxide is treated with some solvent, such as an ammoniacal or alkaline solution, when the rate of reaction will depend on the concentration of the electrolyte, increasing with it. The saturated solution of cupric hydroxide is unsaturated with respect to the non-polymerised "fresh" cupric oxide, [but supersaturated with respect to the polymerised "aged" cupric oxide, and this will settle out.

From the data contained in this paper and in the author's previous publication, we can calculate the free energy of the reaction :



If one faraday is furnished by the combination



the total chemical effect will be given by the above equation.

Now we know that $\text{Cu} \mid \text{Cu}_2\text{O } N\text{-NaOH} = -0.344$ volt

and $\text{Pt} \left| \begin{array}{c} \text{CuO (aged)} \\ \text{Cu}_2\text{O} \end{array} \right. N\text{-NaOH} = -0.154$ volt,

therefore the *E.M.F.* of the above combination is 0.190 volt, and the free energy change of the reaction concerned

$$\frac{96540 \times 0.19}{4.19} \text{ calories}$$

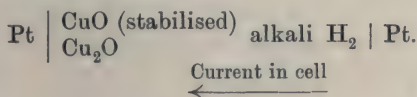
$$= 4370 \text{ calories.}$$

The total energy of the same reaction, calorimetrically determined, is 3600 cals. It should be noticed that, whereas the free energy change is deduced for cupric oxide which has become stabilised at the ordinary temperature, the value of the total energy change used holds for copper oxide which was very probably not stabilised when worked with. The two values are therefore not strictly comparable. It is not, however, likely that the irreversible molecular changes due to polymerisation or depolymerisation at constant temperature are bound up with changes of any magnitude in the total energy of the substance concerned.

This view is borne out by the fact that it is possible to calculate with considerable accuracy the dissociation pressure of cupric oxide at high temperatures from electromotive measurements carried out at the ordinary temperature (see the ensuing calculations), making use of the calorimetrically determined value of the total energy change, and assuming it to be constant over the whole temperature range. By the author's conception, the molecular complexity of the cupric oxide

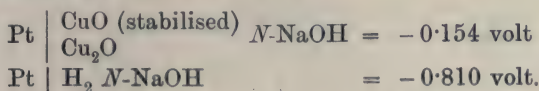
is supposed to change essentially with the alteration in temperature. If this is accompanied by any marked change in total energy, such calculations would not be possible.

Let us next consider the element



It can be regarded as a $\text{H}_2\text{-O}_2$ cell in which hydrogen at atmospheric pressure combines with oxygen furnished at the dissociation pressure of cupric oxide at the temperature in question, and from our data we can calculate this dissociation pressure.

We know that, at 17° ,



Hence the *E.M.F.* of the above cell at 17° is 0.656 volt.

Putting the *E.M.F.* of the $\text{H}_2\text{-O}_2$ cell at 17° at 1.232 volt we get :

$$0.656 = 1.232 + \frac{0.058}{4} \log p_{\text{O}_2}$$

whence $\log p_{\text{O}_2} = -39.7 = \overline{40} \cdot 3$, and p_{O_2} at 17° for $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$ $= 2 \times 10^{-40}$ atmospheres.

By the use of the simple formula (26) given on p. 69 of Haber's *Thermodynamics of Technical Gas Reactions*, we can also calculate the dissociation pressures of cupric oxide at higher temperatures.

Putting in $A=0$, $T=290^\circ$, $R=2$, $Q=67200$, $\log p_{\text{O}_2} = -39.7$, we get : $k = -48.9$.

If we now extrapolate to 1030° (1303° abs.), we obtain

$$\log p_{\text{O}_2} = \overline{1} \cdot 42,$$

or p at 1030° for $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$

$$= 0.26 \text{ atmosphere}$$

$$= 200 \text{ mm.}$$

Experimental determinations by Wöhler and Frey (*Zeitsch. Elektrochem.*, 1909, 15, 34) and by Foote and Smith (*J. Amer. Chem. Soc.*, 1908, 30, 1344) give 170—180 mm. at 1030° . The coincidence falls within the limits of experimental error as far as the electrometric measurements are concerned, and is much better than could be expected, taking into consideration the approximate nature of the calculation involved. This agreement affords additional support to the correctness of the figure -0.154 volt for the equilibrium value at

17° of the electrode potential $\text{Pt} \left| \begin{array}{c} \text{CuO} \\ \text{Cu}_2\text{O} \end{array} \right| N\text{-NaOH}.$

If, on the other hand, we calculate the dissociation pressure of cupric oxide at the two temperatures mentioned from purely thermal data by means of Nernst's well-known formula :

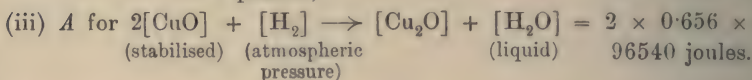
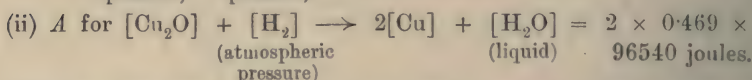
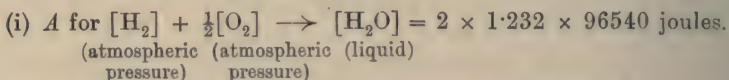
$$(\log. p_{O_2} = \frac{-Q}{4.57 T} + 1.75 \log. T + 2.8),$$

we get at 170° : $p_{O_2} = 2.5 \times 10^{-44}$ atmosphere

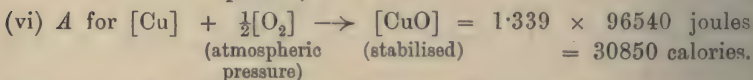
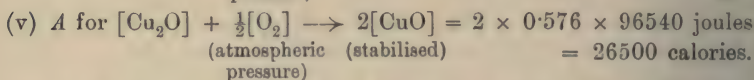
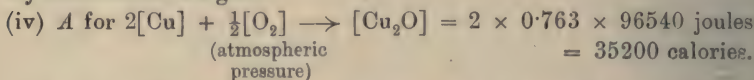
at 1030° : $p_{O_2} = 0.66$ mm.

In both cases the values are far too low, but the discrepancy is considerably greater at room temperature than at 1030° .

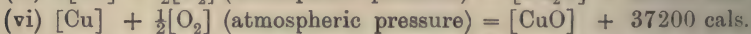
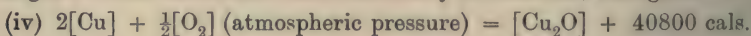
We can also calculate the free energy changes (Δ) for several other reactions. We know that at 17° :



By subtraction we get :



With (iv) and (vi) we can compare the corresponding total energy changes. These have been calorimetrically determined, and gave :



In conclusion, a few remarks may be made concerning a phenomenon noticed by Wöhler in his studies of the thermal dissociation of oxides of copper, palladium, platinum, and iridium (*Ber.*, 1903, 36, 3475; *Zeitsch. Elektrochem.*, 1905, 11, 836; 1906, 12, 781; 1908, 14, 97; 1909, 15, 34). It was sometimes observed that the equilibrium oxygen pressure of a sample of oxide kept at constant temperature did not remain constant, but gradually fell. As the oxides in question were partly decomposed under the conditions of measurement, he attributed this drop in pressure to solid solution formation setting in between the still undecomposed oxide and its solid reaction product. The probability of this explanation being the true one cannot be gainsaid,

but some of his experiments on cupric oxide were also carried out with samples of material which were kept under an excess oxygen pressure until the first reading was taken, and where very little opportunity of cuprous oxide formation was consequently presented. In spite of that fact, high initial values which rapidly fell were noticed, and these values did not represent states of equilibrium as the later ones obtained did, that is to say, if the pressure were slightly increased or decreased, it did not adjust itself again to its original value. Wöhler attributed these pressure changes also to solid solution formation, due to the minimal amounts of cuprous oxide produced, in which case the dissociation pressures of pure cupric oxide would lie higher still. It is quite possible, however, that they may be due to two other causes, as follows :

(1) High initial dissociation pressures given by the finest of the copper oxide particles present. In two samples of oxide microscopically examined by the author, one, prepared from copper nitrate, proved to have a large number of particles down to $1-2\mu$ in size, and the other, made from copper hydroxide by dehydration with ammonia at 25° , consisted to a great extent of particles of dimensions less than 0.5μ . In both cases the solubility in aqueous solutions of the particles would be affected by their size ; and Schoch (*Amer. Chem. J.*, 1903, 29, 319) has further shown, experimentally, that the initial dissociation pressure given by yellow mercuric oxide, with its large proportion of very finely-divided material, greatly exceeds for that reason the pressures given by the red oxide, or by the yellow oxide which has been heated for some time.

(2) According to the conception which has been used to explain the experimental results of this paper, freshly prepared copper oxide will always contain an excess of the less complex molecules, and will therefore have a higher dissociation pressure than a copper oxide in which the different molecular species have come to equilibrium. This circumstance may be the cause of the lowerings of pressure mentioned.

It is also possible that the same cause may bring about the very rapid fall of the initial dissociation pressure which was sometimes noted by Wöhler during his experiments with iridium dioxide. They were ascribed by him to the presence of the unstable iridium sesquioxide.

In any case, isolated examples apart, the variations in potential shown by an electrode system containing samples of copper oxide which have been subjected to varying thermal treatment must, undoubtedly, have their counterpart in variations in oxygen dissociation pressures determined at higher temperatures ; and under suitable experimental conditions, there is no doubt that such effects could be

isolated and studied. If not avoided they will certainly seriously affect dissociation and affinity measurements, although less so than at low temperatures, owing to the more rapid setting up of equilibrium.

It will perhaps be objected that the possibility of solid solution formation is not excluded from the author's measurements. The likelihood of such a complication is very small. None of the copper oxides worked with could be affected before measurements were started—they were never heated above 1000° , at which temperature their dissociation pressure is less than 100 mm., and particular care was taken thoroughly to ignite those samples which were made from cuprous oxide. We should need some positive evidence before admitting the possibility of the formation of solid solution during the measurements, at such a low temperature, and with the very small Cu^{++} and Cu^{+} ionic concentrations in the electrolyte. Moreover, the different initial values given by different samples of oxide would not be thereby explained.

Summary of Results.

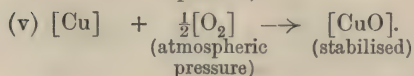
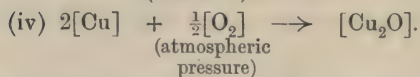
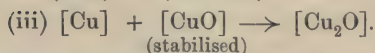
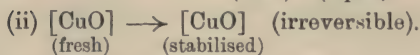
(1) Freshly prepared cupric oxide *ages* with time, and its free energy content thereby falls.

(2) This ageing is attributed to increasing molecular complexity, not to crystallisation or to surface changes.

(3) The explanation given accounts qualitatively for the electromotive behaviour of samples of copper oxide which have been subjected to varying thermal treatment, and may perhaps cast some light on phenomena noticed in the determination of dissociation pressures of certain oxides at higher temperatures.

(4) By means of tensimetric and electrometric measurements, it has been shown that crystalline cupric hydroxide is stable with respect to freshly prepared cupric oxide, and unstable with respect to old samples of cupric oxide.

(5) The decreases of free energy involved in the following reactions have been measured or calculated for 17° .



(6) The dissociation pressure of cupric oxide at 1030° has been calculated and found to agree satisfactorily with experimental results.

The author wishes, in conclusion, to offer his sincere thanks to Professor Donnan for advice and criticism received during the progress of this work.

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LXII.—*Solubilities Below and Above the Critical Temperature.*

By DAN TYRER.

It was first observed by Hannay and Hogarth in 1879 (*Chem. News*, 40, 256) that a solution of a salt, when heated to a temperature above the critical point of the solution, does not necessarily deposit the dissolved salt on the disappearance of the liquid phase. They showed, for example (*Chem. News*, 1880, 41, 103) that a solution of potassium iodide in ethyl alcohol could be heated to a temperature of about 100° above the critical temperature of the solution without the deposition of the dissolved salt.

Pictet (*Compt. rend.*, 1895, 120, 26) heated solutions of borneol, cineol, and terpineol in ether to temperatures above the critical point without the precipitation of any of the solute.

P. Villard (*Chem. News*, 1898, 78, 297, 309) found that easily volatile solids, like iodine and camphor, will dissolve appreciably at the ordinary temperature in compressed gases, such as oxygen and methane.

Centnerszwer and Tetelow (*Zeitsch. Elektrochem.*, 1903, 9, 799) have made some interesting experiments on the solution of anthraquinone in liquid sulphur dioxide; they found that if a certain quantity of anthraquinone is heated in a sealed tube with a particular quantity of liquid sulphur dioxide, the following phenomena occur:

(1) The liquid expands and then diminishes in volume, owing to evaporation, until all the liquid just disappears at temperature t_1 .

(2) As the temperature rises further, the quantity of anthraquinone left undissolved diminishes, and then liquid reappears at temperature t_2 .

(3) The solid anthraquinone passes entirely into solution in the liquid at temperature t_3 .

(4) The liquid phase finally disappears at temperature t_4 .

Obviously in the above, the solubility of the anthraquinone in the vapour of the sulphur dioxide increases with rise of temperature. Centnerszwer and Tetelow made a few measurements of solubility in a mixture of the liquid and vapour of the sulphur dioxide, but the results are not of much interest here. The solubility would be due to a large extent to the mere mechanical mixing of the vapour of the anthraquinone with the sulphur dioxide.

The above experiments show clearly that the phenomenon of solution is not peculiar to the liquid state, but, under certain conditions, the vapour of a liquid may dissolve solids in the same manner as a liquid solvent.

As no quantitative measurements of such solubilities seem to exist, it appeared to be of interest to make some determinations. In commencing this work I had the following objects in view:

(1) To determine the solubility of some non-volatile salts in liquid solvents from the ordinary temperature to the critical point.

(2) To continue the solubility curve through and beyond the critical point, and to find if there were any discontinuity at the critical point.

(3) To determine the solubility in the vapour above the critical point under different conditions of temperature and density of the solution.

Method of Experiment.

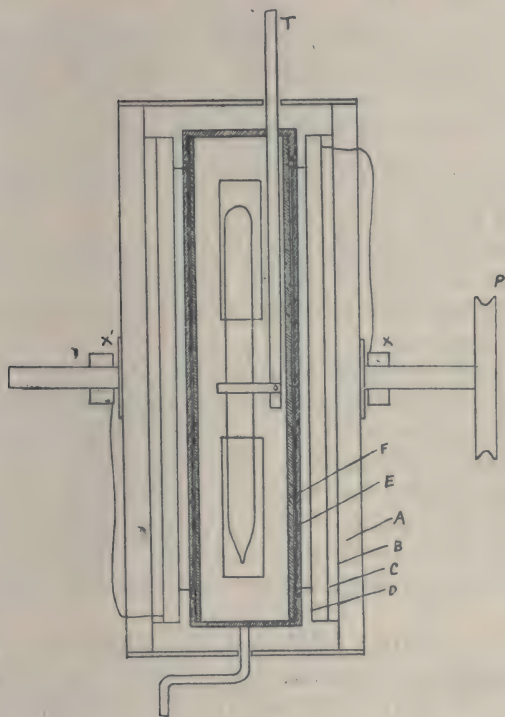
There seems to be only one practicable method of determining solubilities at high temperatures near the critical point. This method is the indirect one of starting with a mixture of the solvent and solute in known proportions and determining, by slowly raising the temperature, the minimum temperature of complete dissolution. Obviously this method is most accurate when there is a moderate change of solubility with change of temperature, and least accurate when this change is very small. The efficiency of the method does, of course, depend largely on the general efficiency of the apparatus and details of working.

Apparatus.

The sealed tubes containing the mixture of solute and solvent were heated in a specially constructed, electrically heated air-bath. This consists (see Fig. 1) of a series of cylinders, *A*, *B*, *C*, and *D*, made of sheet-iron. The cylinder *C* is wrapped closely with thin iron wire (diameter 0.5 mm.), which conducts the current and heats the bath. It is insulated from the metal cylinder by a wrapping of asbestos paper. The heat radiates first to cylinder *F*, and then to a thick ($\frac{1}{4}$ inch) iron cylinder *E*, in which fits closely, but loosely, another iron cylinder

F , of the same material. Through all the cylinders are cut two pairs of opposite windows. By the handle at the side, the innermost cylinder, F , can be turned and the windows shut off. This serves the double purpose of keeping the temperature in the interior more uniform, and also of protecting the apparatus from damage by a bursting tube. On to the ends of the cylinder, F , can be screwed thick iron caps, through one of which passes a thick iron tube, T , which carries a thermometer. The sealed glass tubes are held in the interior by a clip to the tube T ,

FIG. 1.



and the ends of the sealed tube are visible through the windows. The tube T can, moreover, be raised or lowered by a screw, and thus any portion of the sealed tube brought into view. To prevent external loss of heat as much as possible, the space between cylinders A and B is packed with asbestos wool, and the windows in these cylinders are fitted with panes of glass. The terminals of the heating wire are brought to two insulated copper cylinders, X , X' , forming sliding contacts with thick brass wires through which the current is brought. The ends of the outermost cylinder, A , are covered by sheet-iron

plates, to which are fastened disks of asbestos board. The whole apparatus is mounted on stands, and rotated on the pivots by means of a small motor attached by a rope to the pulley *P*. This serves the double purpose of agitating the liquid and salt inside the sealed tube, and of destroying convection currents of air in the interior of the bath and thus ensuring uniformity of temperature.

This bath gives very good results. By varying the external resistance to the current, the temperature can be varied from the ordinary temperature to 400° , or can be maintained constant for any length of time to 0.1° at low temperatures and to about 0.3° at high temperatures (350°).

The sealed tubes were made from glass tubing, the thickness of the walls of which varied from about 2.0 mm. to 4 mm. The capacity of the tubes was, on the average, about 30 c.c. The strength of sealed tubes depended largely on good clear glass free from surface scratches, and, of course, on the thickness and diameter. Tubing more than 4 mm. thick, and of a moderate diameter, was inconvenient to work in the blow-pipe flame.

The thermometers used were mercury thermometers reading to 0.1° , but at high temperatures it was not found practicable to read to less than 0.25° . They were carefully graduated by comparison with a standard thermometer.

It was found necessary in preparing the tubes to introduce particular quantities of the solvent and solute, so as to give a particular percentage concentration when saturated. Direct weighing of the solvent became, on this account, impracticable, and the solvent was, therefore, run out of a very carefully graduated burette consisting of a narrow tube with capillary exit-tube, which could be projected into the open end of the tube that was being prepared. In reading the volume of the solvent added, correction was made for room temperature.

Sodium Iodide and Ethyl Alcohol.

The sodium iodide was purified in the ordinary way by recrystallisation from a mixture of distilled water and alcohol. The last traces of moisture were removed by placing the partly dried salt in a bulb-tube and heating in a current of air until constant in weight.

The ethyl alcohol was commercial "absolute" alcohol, from which the last traces of water were removed by repeated treatment with sodium followed by fractional distillation. In order to prove that no reaction took place between the sodium iodide and the alcohol at a high temperature, a solution containing a known weight of sodium iodide was heated in a sealed tube to 300° for several hours. After cooling, the contents of the tube were analysed, when the original quantity of sodium iodide was found to be present.

The sealed tubes were prepared as follows : A selected piece of glass tubing was carefully and thickly sealed at one end, and drawn out to a narrow constriction a few inches from the other end. The capacity of the tube was then ascertained by running in mercury from a burette to a point in the constriction where the tube was subsequently sealed off. The tube was then cleaned and dried, and the requisite amount of sodium iodide added from a weighed bulb-tube having a long tube as neck, which was projected into the open end of the tube being prepared. To prevent an explosion in the tube between the air and the alcohol vapour when sealing off, the air was displaced by dry carbon dioxide. As a rule, the tubes were not evacuated, except those heated to the higher temperatures. The presence of a small quantity of carbon dioxide was found, by blank experiments, not to affect the solubility to any measurable extent. The requisite amount of alcohol was then added from the burette, and the tube then sealed off at a point in the constriction.

In preparing a tube for a determination of the solubility in the liquid at a high temperature, where the density of the vapour is quite appreciable, it was necessary to add such an amount of alcohol that by thermal expansion the amount of liquid existing in the state of vapour at the temperature of the determination would be negligibly small.

To a certain point it was found that the solubility increased with rise of temperature, and in determining a minimum temperature of dissolution within this range, the temperature was first raised quickly and a rough idea of the dissolution temperature obtained. Then the tube was cooled to about five degrees below this point, and raised very slowly with constant rotation of the bath until the point was found at which the last trace of salt just dissolved. The whole experiment required, on the average, between four and five hours.

At a higher temperature the solubility was found to decrease with rise of temperature, and in this case the temperature was raised quickly until some salt separated from the solution. The temperature of dissolution was then found as before, but by cooling instead of heating.

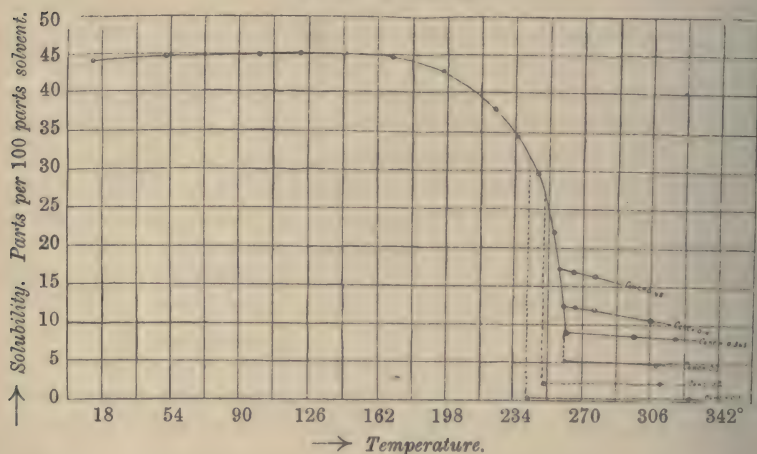
If the amount of alcohol added exceeded a certain critical quantity, then before the critical temperature was reached the solution expanded and filled the tube completely. At this point there was a break in the curve and a new curve began. Similarly, if the amount of alcohol added fell short of this critical quantity, the liquid would diminish in quantity, and, finally, all be vaporised before the critical point was reached. Again, there was a break in the solubility curve, and a new curve of solubility in the vapour began.

Results.

The numerical results of the solubility of sodium iodide in liquid alcohol from the ordinary temperature to the critical point are given in the following table. The values are calculated from a carefully drawn and smoothed curve of the experimental results, which are indicated in Fig. 2.

FIG. 2.

Solubility of sodium iodide in ethyl alcohol from ordinary temperature to temperatures above the critical point.



Solubility of Sodium Iodide in Liquid Ethyl Alcohol from the Ordinary Temperature to the Critical Point.

Tempera- ture.	Solubility. Parts by weight of sodium iodide dissolved in 100 parts of ethyl alcohol.
10°	43.77 ± 0.04
30	44.25 ± 0.10
50	44.50 ± 0.05
80	45.0 ± 0.1
100	45.1 ± 0.1
120	45.2 ± 0.1
160	45.0 ± 0.2
180	44.3 ± 0.2
200	42.8 ± 0.3

Tempera- ture.	Solubility. Parts by weight of sodium iodide dissolved in 100 parts of ethyl alcohol.
220°	38.5 ± 0.3
230	36.2 ± 0.4
240	32.7 ± 0.4
250	26.2 ± 0.5
255	21.0 ± 0.8
260	10.8 ± 0.8
261.5	8.6 ± 0.05

(Critical temperature
of solution)

The probable accuracy of the numbers is appended. From 250° to 261.5° there is an enormous fall in the solubility, and the accuracy of the determinations in this range is much impaired on this account. The point at which the meniscus of a saturated solution just dis-

appears is 261.5° . This, it will be noticed, is very considerably higher than the critical point of the pure solvent. On reference to the curve (Fig. 2) it will be noticed that the solubility increases with rise of temperature to about 140° , and then decreases, at first slowly and then more rapidly, until the curve becomes almost vertical. At 261.5° the liquid phase ceases to be distinguishable from the vapour, and here there is a break in the solubility curve. This discontinuity is more apparent than real, as will be pointed out later. In order to show the phenomenon of the slow disappearance of the meniscus, a tube of given volume must contain approximately a definite amount of solvent. The amount of solvent contained in a tube of given volume is expressed in terms of the concentration of the solvent when all the liquid has disappeared, that is, the amount of solvent contained in unit volume. The critical concentration was found to be 0.365, but this figure is only approximate, as the point is very indistinct, concentrations of 0.370 and 0.360 both giving the critical phenomenon of the slow disappearance of the meniscus. If the concentration of the solvent exceeds 0.365 gram per c.c., the liquid will expand and fill the tube entirely. If the concentration of the solvent is, for example, 0.45 gram per c.c., the saturated solution will just fill the tube completely at 255° , and at this point there is a break in the curve, and, on continuing, the almost horizontal curve indicated is obtained. Similarly, a solution of concentration of the solvent of 0.4 gram per c.c. fills the tube completely at 259° , and another curve branches out, which it will be noticed has a smaller gradient than that of concentration 0.45. The critical curve of concentration 0.365 slopes still less. If now the concentration of the solvent is below the value 0.365, the liquid boils away before the critical point is reached. If, for example, the concentration is 0.1 gram per c.c., the liquid just completely evaporates at 242° , and then there is a drop in the solubility from 31.9 per cent. in the liquid to about 0.5 per cent. in the vapour. Temperature up to about 325° has no measurable influence on the solubility in the vapour of this particular concentration. A solution of concentration of the solvent of 0.2 gram per c.c. also gives a curve parallel to the abscissa; the curve of concentration 0.3 has a very slight gradient.

The numerical results of the solubility in the vapour at varying conditions of temperature and concentration are given in the following table. The numbers express parts by weight of sodium iodide which dissolve in 100 parts of ethyl alcohol.

Solubility of Sodium Iodide in the Vapour of Ethyl Alcohol above the Critical Point.

Temperature.	Concentration of the Solvent.						
	0.1	0.2	0.3	0.365	0.4	0.45	0.48
262°	0.5±0.1	2.1±0.1	5.1±0.05	8.6±0.05	11.6±0.1	17.3±0.2	21.6±0.4
270	"	"	5.1	8.35	11.5	17.0	—
280	"	"	5.0	8.2	11.0	16.5	—
290	"	"	4.9	8.0	10.5	—	—
300	"	"	4.8	7.7	10.2	—	—
310	"	"	4.7	7.5	9.7	—	—

The above figures are calculated from the smoothed curves of observed results. The probable accuracy in the first series at 262° is appended. The accuracy of the remaining numbers is only comparative, that is, it depends on the accuracy of the first series.

Determinations in the vapour were very difficult to make. Owing to the homogeneity of the solvent above the critical point, the mixing of the solvent and solute was less efficient than in the liquid state, where the solvent was not wholly homogeneous. The salt had, moreover, a peculiar aptitude for crystallising on the sides, but this difficulty was largely overcome by placing in the tubes small pieces of platinum foil, which, falling up and down the tube, assisted the dissolution. It was found that the process of dissolution in the vapour was much accelerated by keeping the temperature at the point at which the liquid disappeared, so that the undissolved salt remained moist, and the saturated liquid solution would completely evaporate without deposition of the dissolved salt. The following way of testing whether the solution in the vapour was saturated or not proved very useful. If the bath were kept vertical for a short time, the upper part of the tube would become slightly hotter than the lower part, with the result that the vapour within the tube would expand locally, and, if saturated, would deposit a thin, crystalline film of salt on the sides of the hotter portion of the tube. Indeed, it was possible in this manner to distil the solid salt from one portion of the tube to another. It was found impossible to continue the determinations above about 310°, for, in order to ensure a fair degree of accuracy, it was necessary to use fairly large tubes, so as to hold moderate amounts of the solvent and solute, and with increase in size of the tube, the strength decreased.

The curve of solubility in the vapour at 262° showing the relation between solubility and concentration of the solvent is given in Fig. 3.

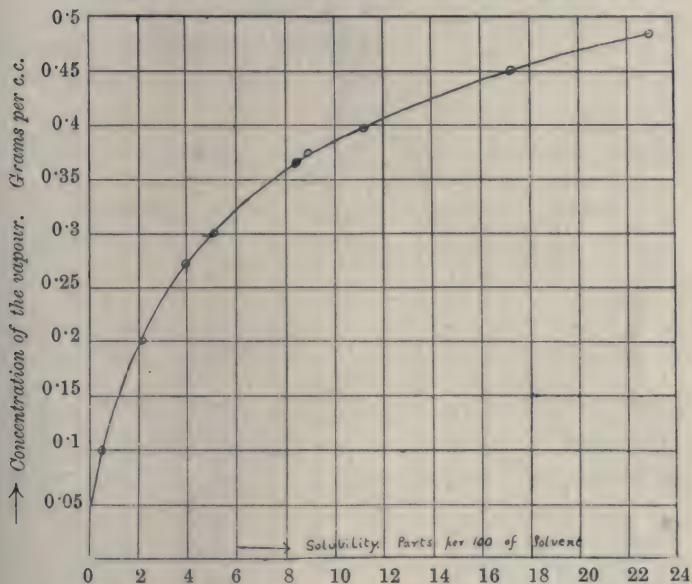
It will be noticed that the solubility diminishes regularly with decrease of concentration, becoming practically zero at a concentration of about 0.05 gram per c.c.

Potassium Iodide and Methyl Alcohol.

The potassium iodide was purified by recrystallisation, and completely freed from traces of moisture by heating in a bulb-tube in a current of air until constant in weight. The methyl alcohol was the commercial "absolute" alcohol, which was freed from last traces of

FIG. 3.

Solubility curve of sodium iodide in vapour of ethyl alcohol at 262°.



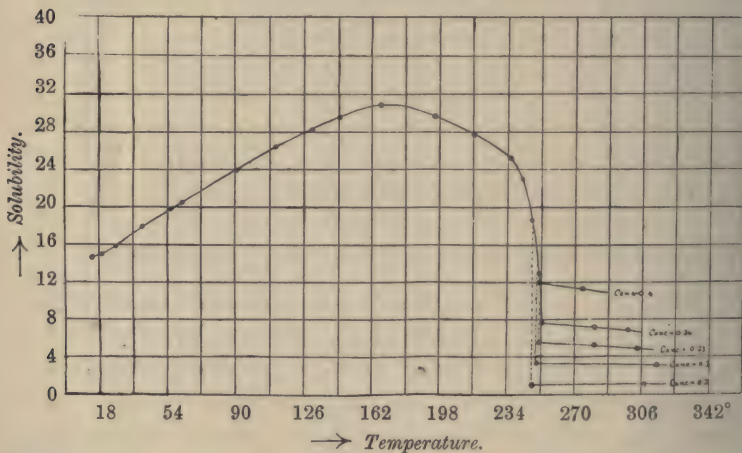
water by keeping it over excess of anhydrous copper sulphate for a fortnight, and then fractionally distilling. A sample, kept for months afterwards in a sealed tube with a little anhydrous copper sulphate, did not affect the colour of the latter, although it dissolved a little to a blue solution. The general method of investigation was the same as in the previous case, and it is only necessary to give here the numerical results and curves. No reaction was found to take place between potassium iodide and methyl alcohol even at 300°.

Solubility of Potassium Iodide in Liquid Methyl Alcohol from the Ordinary Temperature to the Critical Point.

Temperature.	Solubility. Parts per 100 of methyl alcohol.	Temperature.	Solubility. Parts per 100 of methyl alcohol.
15°	14.50 ± 0.05	200°	29.1 ± 0.2
30	16.20 ± 0.05	220	27.5 ± 0.2
50	18.9 ± 0.06	240	24.8 ± 0.3
80	22.5 ± 0.08	245	22.6 ± 0.5
100	25.0 ± 0.1	247	21.0 ± 0.5
120	27.2 ± 0.1	250	13.8 ± 0.6
140	29.2 ± 0.15	252.5	7.6 ± 0.1
160	30.6 ± 0.2	(Critical temperature of saturated solution)	
180	30.7 ± 0.2		

FIG. 4.

Solubility curve of potassium iodide in methyl alcohol from ordinary temperature to 310°.



The above figures are calculated from a smoothed curve of experimental numbers. The probable accuracy is appended. The critical concentration of the solvent was found to be about 0.36, but this point is even more indistinct than in the previous case. The above results are shown graphically in the curve in Fig. 4. It will be seen that the solubility first increases to about 170° and then decreases. The rate of decrease during the range 240—250° is exceedingly great. The rest of the curve will be easily understood from the explanation given in the case of sodium iodide and ethyl alcohol.

The numerical results for the solubility in the vapour are given in the following table.

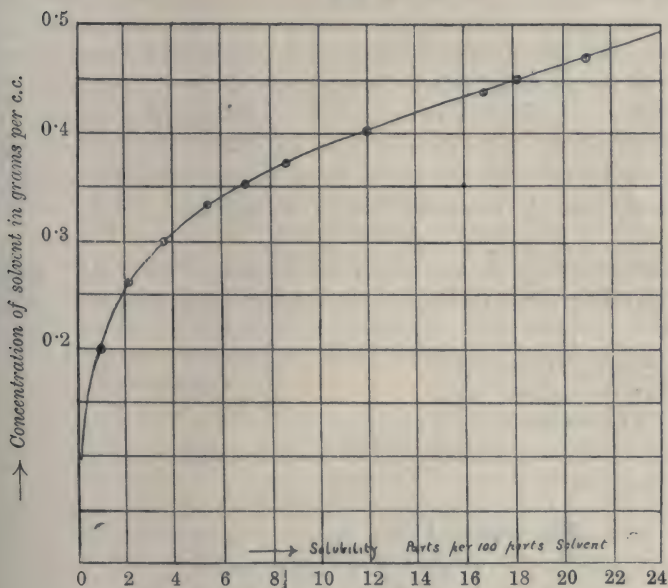
Solubility of Potassium Iodide in Vapour of Methyl Alcohol above the Critical Point.

Temperature.	Concentration.					
	0.1	0.2	0.3	0.36	0.4	0.45
252°	<0.3	1.0±0.05	3.7±0.1	7.6±0.1	11.8±0.1	18.1±0.2
270	—	„	3.5	7.4	11.5	—
280	—	„	3.4	7.3	11.3	—
290	—	„	3.4	7.2	11.0	—
300	—	„	3.3	7.0	—	—

The above figures represent the solubility in parts by weight dissolved in 100 parts of the solvent.

The accuracy of the numbers beyond the first series is dependent on

FIG. 5.



the accuracy of the numbers in the first series; the relation between the solubility in the vapour at 252° and the concentration of the solvent is shown in the curve in Fig. 5. The curve is similar to that obtained in the case of sodium iodide and ethyl alcohol.

Discussion of Results.

The first and most interesting point to notice is that the solubility in the vapour is a function of concentration of the solvent. An extension of this idea to the liquid state explains the very great and

rather sudden fall of solubility in the liquid just below the critical temperature. For over this range the rate of expansion of the solution is very much greater than at lower temperatures. It also explains the apparent discontinuity in the solubility curve at the critical point, for just previous to the critical point the solvent has been undergoing a great decrease in concentration, and when this point is reached this decrease, of course, stops and the concentration of the solvent remains practically constant (the slight expansion of the glass being neglected), with the result that the solubility remains nearly constant. If we imagined the concentration of the solvent to decrease past the critical point at the same rate as before, and if we plot the solubilities for the concentrations thus obtained, we get no discontinuity at the critical point, but a perfectly uniform curve.

The second point to notice is that the solubility in the vapour decreases with rise of temperature, although the concentration remains constant, and, further, that this decrease is greater for the greater concentrations of the solvent. This would suggest the formation of hydrates in the solution which dissociate under the influence of heat. If the process of solution is due to an attractive force between the molecules of solute and solvent, then we should expect, as is here found to be the case, that the solubility at constant temperature would vary directly with the concentration of the solvent.

In conclusion, I desire to express my thanks to Prof. H. B. Dixon and Dr. A. Lapworth for much kind advice and interest taken in the work.

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LXIII.—*A Supposed Case of Stereoisomeric Tervalent Nitrogen Compounds.*

By HUMPHREY OWEN JONES and EDWARD JOHN WHITE.

IN 1896 (*Ber.*, **29**, 1462) von Miller and Plöchl described two isomeric compounds, $C_{12}H_{17}ON$, obtained by the interaction of *m*-4-xylydine and acetaldehyde in dilute hydrochloric acid solution: these differed in crystalline form, melting point, solubility, and stability. The more soluble and more fusible form, melting at 102° , hereinafter called the α -form, was partly converted into the β -form, melting at 131° , by crystallisation from solvents, by solution in acids, or by heat. Both compounds gave the same oxime, benzoyl

derivative, and condensation product, $(C_{10}H_{13}N)_2$, with xylidine, also the same 2: 6: 8-trimethylquinoline was obtained from both.

The two isomeric compounds were therefore considered to have the same structural formula, namely, $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, and it was suggested that they differed only in the disposition of the three groups around the tervalent nitrogen atom.

It is remarkable that the observations on this interesting case of isomerism have not been extended, especially on account of its important bearing on the stereoisomerism of nitrogen.

The present paper contains a short account of a re-investigation of these compounds, and of the preparation of similar compounds from other amines.

The method of preparation has been improved, and it has been found that the properties of the compounds agree generally with those described by Miller and Plöchl, but with the important difference that *neither isomeride is transformed into the other by the action of solvents or of heat*. This fact renders the hypothesis of stereoisomerism untenable, but the nature of the isomerism is still a problem of general interest.

Although no transformation is effected by heat or inert solvents, it is brought about readily by the action of acids. In dilute acid solution the α - and β -forms are converted into the same equilibrium mixture, consisting of approximately two parts of the α - to one part of the β -compound, which is also the composition of the mixture obtained in the preparation of the substances in the first instance: this equilibrium mixture in acid solution changes into 2: 6: 8-trimethylquinoline, slowly at the ordinary temperature, and rapidly on heating.

In addition to yielding the same oxime, benzoyl derivative, and condensation product with xylidine, the two isomerides gave the same benzylphenylhydrazone and the same methyl derivative, $C_6H_3Me_2 \cdot NMe \cdot CHMe \cdot CH_2 \cdot CHO$.

The only difference in chemical properties which the two compounds have been found to exhibit is in their behaviour towards hydrogen chloride and towards nitrous acid. When a solution of the α - or β -compound in ether or benzene was treated with hydrogen chloride, a compound of the composition $C_{12}H_{17}ON, HCl$ was precipitated in each case; that from the α -form melts at 85° , whilst that from the β -form melts at 135 — 136° , and is identical with the product obtained by the action of aqueous hydrochloric acid.

The difference in the products of the interaction of the two compounds and nitrous acid is remarkable; both compounds yielded a non-basic substance which gave Liebermann's nitroso-reaction; but whereas the product obtained from the β -form was

crystalline and had the composition $C_{12}H_{16}O_2N_2$, that from the α -form was oily and could not be obtained pure.

The absorption spectra of the two forms have been examined, and the curves obtained are very nearly but not quite identical.

Similar isomeric compounds have been prepared from *p*-toluidine and ψ -cumidine.

As regards the cause of this case of isomerism, it is clear that the α - and β -compounds cannot be stereoisomeric, since each is too stable towards heat, and under the influence of solvents, and of two compounds differing only in the disposition of the groups around the tervalent nitrogen atom, one would inevitably be very unstable. Yet any structural difference between the compounds must be slight and easily removed, since so many derivatives are identical, and the absorption spectra are so nearly the same. In all cases the α -compound is distinctly more reactive than the β -compound, but in two cases only are the derivatives of the two isomerides different, namely, the hydrochlorides and nitroso-compounds.

The adoption of the formula $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$ for the α -compound, and

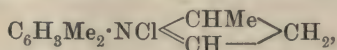


for the β -compound, affords a satisfactory explanation of all the facts observed, with the exception of the action of nitrous acid.

The hydroxytrimethyleneimine ring present in the β -compound would be unstable, especially towards acids, just as the trimethyleneimine ring has been found to be (Howard and Marckwald, *Ber.*, 1899, **32**, 2031), and under the influence of acids or other reagents would undergo fission, so that the product obtained from the β -compound with hydroxylamine, benzoyl chloride, benzylphenylhydrazine, or methyl iodide would be identical with that obtained from the α -compound.

Certain suggestions might be made to account for the different products obtained by the action of nitrous acid, but the experimental evidence is insufficient to discriminate between them. Both compounds are insoluble in acids, so that it is improbable that either is an ester or a salt.

The products obtained with hydrogen chloride would be the simple additive products, different for the α - and β -forms: there is no evidence of the formation of an ammonium salt of the type



similar to that formed from cotarnine (Dobbie, Lauder, and Tinkler, *Trans.*, 1903, **84**, 598).

EXPERIMENTAL.

The method given by Miller and Plöchl for obtaining the mixture of the two isomeric compounds consists in mixing xylidine, dilute hydrochloric acid, and acetaldehyde, keeping the mixture for one day, and then fractionally neutralising it. A dark resinous substance is first formed, and is removed, after which a red oil, representing the isomeric mixture, separates. This is extracted with ether, and the crystalline product is obtained from the ethereal solution after concentration, part of it by addition of light petroleum, and the remainder by keeping the gummy mother liquor for some days, when a further crop of crystals separates. In this way 20 grams of xylidine yield 17 grams of yellow, solid product.

Several difficulties were encountered in repeating the preparation as above described. There is no definite stage in the neutralisation of the acid solution to separate the resinous from the oily precipitates, and in reality a complicated succession of precipitates of different degrees of colour and consistency is obtained. Consequently, either the yield of solid product is small, owing to the greater part of the crystalline material having been removed along with the "resin," or less "resin" is separated and the crystalline material is only very slowly obtained from the impure ethereal solution. Moreover, in addition to the two crystalline, isomeric substances, and to the dark-coloured, uncrystallisable substance, which is probably ethylidenexylidine, $C_6H_3Me_2N:CHMe$, a third crystalline substance is invariably present in the product, the so-called bimolecular ethylidenexylidine, $C_{20}H_{26}N_2$. Miller and Plöchl seem to have overlooked its presence, but it is formed in considerable quantity, 20 grams of xylidine yielding about 4 grams, and of this amount a large proportion must inevitably have been present in their 17 grams of crude product.

It was found possible, however, by modifying the original method of preparation to overcome both difficulties simply and successfully, and thus obtain a better yield of the product as a white, crystalline solid. The modified process depends on the fact that both the coloured, uncrystallisable impurity and the bimolecular ethylidenexylidine are soluble in light petroleum and dissolve very readily if the light petroleum is present at the time of their precipitation, whereas the isomeric substances are only very sparingly soluble in the cold solvent. The method is as follows.

Xylidine (10 grams) was poured into Erlenmeyer flasks containing twice the equivalent quantity of hydrochloric acid diluted with water to 120 c.c. A slight excess (11 c.c.) of acetaldehyde was

added, and the mixture kept in the stoppered flasks at the ordinary temperature for at least eighteen hours.* About 40 c.c. of light petroleum were now added, and the requisite amount of alkali for complete neutralisation was poured in quickly, the flask being vigorously shaken. The red petroleum solution contained the impurities, and after a few minutes the isomeric mixture separated as a white, crystalline cake on the surface of the water-layer. The solid product was collected, washed with light petroleum and water, and dried.

The crystalline mixture, 12 grams of which are thus obtained from 10 grams of xylidine, melts at 84–87°, and consists approximately of 8 grams of the α - and 4 grams of the β -isomeride. The composition in this and other cases is approximately deduced from the residue of β -compound left after extracting the more soluble α -compound from a weighed quantity of the mixture, allowance being made for the β -compound, which is removed at the same time.

Miller and Plöchl obtained the less soluble β -form by fractional crystallisation from ethereal solution and the α -form by mechanical separation. The following method was found much more suitable for the preparation of the β -compound. The amount of benzene required to dissolve the more soluble component was added to the mixture (60 c.c. of benzene for 12 grams of mixture), and after shaking for about half an hour, the solid residue was removed by filtration. After one recrystallisation from benzene, nearly 4 grams of pure substance were obtained.

The α -isomeride is very difficult to separate in a state of purity. The method of mechanical separation is unsuitable for obtaining large quantities of the pure substance. This is chiefly because neither compound shows much tendency to crystallise in large individual crystals. Various solvents were tried, and many modifications were made in the conditions of crystallisation and separation, but in every case only a very small proportion of each product consisted of separable crystals. Even under the most favourable conditions the crystallised mixture is mainly made up of masses which consist of radiating clusters of both kinds of crystals, and cannot be detached so as to admit of mechanical separation. For the same reason, although there is an appreciable difference of density, namely, 1.13 and 1.19 for the α - and β -forms respectively, the method of separating by means of a liquid of intermediate density was also unsuccessful. Since, as will be seen later, the α -form is not transformed by the action of inert solvents,

* Longer keeping than eighteen hours, even for several days, has no further influence on the nature or quantity of the products.

it should be possible to separate it by fractional crystallisation. Repeated crystallisation from various solvents never gave specimens with a higher melting point than $96\text{--}99^\circ$, whereas the pure α -compound melts at $103\text{--}104^\circ$. The explanation of this undoubtedly lies in the relative solubilities of the two compounds. The solubilities in various solvents, including benzene, ether, acetone, and alcohol, were determined, and it was found that, in each of these cases, the ratio between the solubilities of the compounds has very nearly the same value, namely, about 4:1. It follows that the more soluble component cannot be purified by a simple process of crystallisation until a solvent is found for which the two solubilities are either more nearly equal or more discrepant than they are in the above cases. The difficulty caused by this accidental uniformity in the relative solubility of the two isomerides has not yet been overcome. At present the only means of obtaining the pure α -compound is by mechanical separation followed by crystallisation; this is very slow and tedious, but enough of the pure α -compound has been obtained in this way to allow of an investigation of its properties.

Melting Point.—The melting points given by Miller and Plöchl are 102° and 131° for the α - and β -compounds respectively. It is now found that the α -form melts at $103\text{--}104^\circ$, and the β -form at $127\text{--}128^\circ$. In both cases, especially the former, the melting point is much affected by the presence of impurity. It is noteworthy, in connexion with the question of transformability, that the melting point of individual rhombohedral crystals picked out from the crystalline mixtures is never more than $99\text{--}101^\circ$, and is usually considerably lower; therefore, after mechanical separation, the crystals of the α -compound must be recrystallised before the substance can be obtained quite pure.

Crystalline Form.—The crystals of the α -isomeride have commonly a rhombohedral appearance, but are often elongated, and are then not so easily distinguished from those of the β -form. The latter are flat needles, differing from the former in possessing marked cleavage, the cleavage fragments being diamond-shaped. Both kinds of crystals occur usually as radiating clusters of small individuals.

Solubility.—The α -compound is easily soluble in acetone, benzene, ether, or alcohol, these solvents being arranged in descending order of solubility. It is very sparingly soluble in cold, but moderately so in hot light petroleum, and insoluble in water. It is readily soluble in dilute acids. The solubility of the β -isomeride, as already stated, is in all these cases proportionately less, the ratio being very nearly constant at 1:4.

Absorption Spectra.—These were observed by Mr. J. E. Purvis, and are described in the paper following this. The curves for the two isomerides are very nearly but not quite identical. The spectra of the corresponding *p*-toluidine derivatives, the preparation and properties of which are described later, show very clearly a difference of precisely the same nature as that observed in the xylidine derivatives.

It is impossible to draw very definite conclusions from these results as to the constitution of the two compounds, but it is extremely probable that two substances, with absorption spectra so nearly the same, would only differ slightly in chemical constitution.

Transformability.—Miller and Plöchl state that the β -compound is stable, but that the α -compound is "partly" transformed into the other form by (i) simple crystallisation from solvents; (ii) keeping in acid solution for some time; (iii) heating above its melting point. It was found that no transformation could be effected either by solvents or by heat.

In addition to showing that the pure α -compound could be recrystallised several times without changing the melting point, the following more stringent experiments were made. Solutions of the purified substance, melting at 103–104°, in different solvents, such as benzene or light petroleum, were heated to 100° in sealed tubes for several hours, after which the substance was recovered absolutely unchanged.

The effect of heat alone was examined by heating the α -form in an air-oven to 110° (at higher temperatures quinoline formation takes place very rapidly). The substance was then washed with light petroleum in order to remove any trimethylquinoline which had been formed, and the residue again proved to be unchanged substance, melting at 103–104°.

The β -compound was submitted to the same treatment and found to be equally stable.

Action of Acids.—The two compounds are, however, transformed on treatment with acids. The α -form is much more easily dissolved by dilute hydrochloric acid than the β -form, but on keeping in acid solution each form is transformed into an equilibrium mixture, which has the same composition as the mixture obtained when the substances are prepared in the ordinary way by the condensation of xylidine and aldehyde in acid solution. In cold dilute acid the change is slow, needing several days for completion, but on warming the solution, the equilibrium is attained in a few minutes. In all cases when either the α - or the β -compound is dissolved in acid and reprecipitated by the addition of alkali, the

quantity of base recovered is considerably less than the amount dissolved, owing to the formation of 2:6:8-trimethylquinoline, which takes place very readily under the influence of acids.

Action of Hydrogen Chloride.—The α - and β -compounds were dissolved in dry ether or benzene, and dry hydrogen chloride was passed into the solution, when a white precipitate separated immediately.

The α -form yielded a deliquescent product, which sintered at 80° , and melted with frothing at 85° :

0.2755 gave 0.6345 CO_2 and 0.1910 H_2O . $\text{C}=62.8$; $\text{H}=7.7$.

0.2579 „ 0.1654 AgCl . $\text{Cl}=15.8$.

$\text{C}_{12}\text{H}_{17}\text{ON}, \text{HCl}$ requires $\text{C}=63.3$; $\text{H}=7.91$; $\text{Cl}=15.7$ per cent.

The aqueous solution was acid to litmus, and on the addition of alkali an oil separated, which crystallised after some time. The crystals melted at 88° , and were a mixture of the α - and β -forms.

The β -form yielded a white, crystalline precipitate, which melted without decomposing at 135 — 136° , and could be recrystallised from alcohol or water unchanged. The same substance is produced by allowing a solution of the base in aqueous hydrochloric acid to evaporate spontaneously, when it separates in long, needle-shaped crystals:

0.2715 gave 0.6220 CO_2 and 0.1895 H_2O . $\text{C}=62.8$; $\text{H}=7.8$.

0.2855 „ 0.1865 AgCl . $\text{Cl}=16.1$.

$\text{C}_{12}\text{H}_{17}\text{ON}, \text{HCl}$ requires $\text{C}=63.3$; $\text{H}=7.91$; $\text{Cl}=15.7$ per cent.

The aqueous solution, on the addition of alkali, deposited a crystalline solid, which melted at 125° , and consisted of the β -form.

Formation of Trimethylquinoline.—The action of heat or of strong acids is, as stated by Miller and Plöchl, to decompose the compounds with formation of 2:6:8-trimethylquinoline. Thus, if the α -compound is heated to 120° in an air-oven for half an hour and the residue distilled in a current of steam, a 50 per cent. yield of trimethylquinoline will be found in the steam distillate as large, crystalline plates, melting at 45 — 46° . The β -compound requires heating to 150° for about two hours to give a similar yield.

Acids, even when cold and not very concentrated, slowly effect the same transformation, and the change takes place completely if either of the compounds is warmed for a few minutes with concentrated hydrochloric acid. This effect of acids is also illustrated by the action of *d*-camphorsulphonic acid. Dry acetone solutions of the two bases were mixed with dry acetone solutions of *d*-camphorsulphonic acid, with the object of preparing the camphorsulphonates. A crystalline product separated in each case, melting after purification at 229 — 231° , but when examined

was found to be a camphorsulphonate, not of the original bases, but of 2:6:8-trimethylquinoline. If ether is added to the solution immediately after mixing, colourless crystals separate, which melt at a low temperature (about 103°), but these change rapidly into the camphorsulphonate of 2:6:8-trimethylquinoline.

Aldehyde Reactions.—Miller and Plöchl lay stress on the fact that both compounds reduce ammoniacal silver solutions, taking this as indicating their aldehydic nature. The silver reduction does actually take place, but in neither case so readily as that brought about by the simple amines, such as xylidine itself. The test, therefore, is valueless. Both compounds do, however, condense with hydroxylamine, benzylphenylhydrazine, and xylidine, and these condensations will now be described.

Condensation with Hydroxylamine.—The method of preparing the oximes described by Miller and Plöchl was found to give good results. Both compounds give a 60 per cent. yield of the same compound, which, when crystallised from alcohol, melted at $163\text{--}166^{\circ}$, Miller and Plöchl's value being 165° . As the analysis given in the original paper is somewhat unsatisfactory, the following analytical results are appended:

0.1785 gave 0.4570 CO_2 and 0.1450 H_2O . $\text{C}=69.8$; $\text{H}=9.0$.

$\text{C}_{12}\text{H}_{18}\text{ON}_2$ requires $\text{C}=69.9$; $\text{H}=8.75$ per cent.

Since the isomeric compounds are both transformed into a mixture in acid solution, attempts were made to condense them with free hydroxylamine in alcoholic solution. Under these conditions, however, no reaction occurred, and the unchanged bases were isolated.

Condensation with Xylidine.—Both substances can be condensed with xylidine by simply mixing calculated quantities in alcoholic solution, and heating on the water-bath in a sealed tube, or in a flask provided with a reflux condenser. The condensation product is very sparingly soluble in alcohol, and in about three hours, in the case of the α -compound, it separates out as a white, crystalline precipitate, the yield being about 25 per cent. of the theoretical. The β -isomeride gives an equal yield after about six hours' heating. This method of condensation is found considerably quicker and simpler than Miller and Plöchl's method of heating the reagents suspended in a large quantity of water and afterwards proceeding to isolate the condensation product.

The only information available with regard to this condensation compound, the so-called bimolecular ethyridenexylidine, is to be found in a short paragraph in Miller and Plöchl's paper (*loc. cit.*, p. 1467), therefore a few supplementary details are given here. The compound crystallises in isolated, flat, six-sided plates with

vitreous lustre, and melts at 144—145°; Miller and Plöchl give 147°. It is moderately easily soluble in cold light petroleum, thereby differing from the isomeric compounds; it is easily soluble in benzene, ether, or dilute acids, and very sparingly so in alcohol.

No analyses or molecular weight determinations for the condensation product appear to have been published, but it has undoubtedly the formula $C_{20}H_{26}N_2$, as the following results show:

0.2070 gave 0.6185 CO_2 and 0.1660 H_2O . $C=81.5$; $H=8.9$.

0.415, in 17.50 benzene, gave $\Delta t = -0.400^\circ$. M.W.=296.

$C_{20}H_{26}N_2$ requires $C=81.6$; $H=8.84$ per cent. M.W.=294.

Miller and Plöchl assume that the constitutional formula is $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CH \cdot N \cdot C_6H_3Me_2$. Its empirical formula shows it to be a bimolecular polymeride of the simple Schiff's base, $C_6H_3Me_2 \cdot N \cdot CHMe$, and the method of preparation and general properties render the above constitutional formula *prima facie* probable.

In addition to the method of preparation described above, two other methods may be employed. It is formed along with the isomeric bases when xylidine is condensed with acetaldehyde in acid solution, as has already been mentioned, but it is most conveniently prepared by the direct condensation of xylidine with acetaldehyde in alcoholic solution. The calculated quantity of acetaldehyde is slowly added to an alcoholic solution of xylidine at 0°, when the product separates first as a red oil, but in a few minutes solidifies to a yellow mass, which is collected and purified by recrystallisation from alcohol.

The compound is readily soluble in dilute acids, but in acid solution it slowly decomposes into xylidine and the equilibrium mixture of the isomeric compounds, the reaction occurring in the first method of formation being thus exactly reversed. It would therefore appear that, in acid solution, there is an equilibrium between the three substances, bimolecular ethyldenexylidine and the two α - and β -compounds.

Condensation with Benzylphenylhydrazine.—The compounds were dissolved in alcohol, calculated quantities of benzylphenylhydrazine added, and the solutions allowed to evaporate. Gummy residues were left, which crystallised after several days. After crystallising from alcohol, it was found that the same derivative, melting at 120—121°, was obtained from both compounds:

0.1597 gave 0.4725 CO_2 and 0.1148 H_2O . $C=80.6$; $H=7.98$.

$C_{15}H_{29}N_3$ requires $C=80.9$; $H=7.82$ per cent.

Reaction with Benzoyl Chloride.—The reaction with benzoyl chloride takes place readily on adding excess of benzoyl chloride to a benzene solution of either compound in presence of a large excess

of 10 per cent. sodium hydroxide solution. The mixture is shaken vigorously during the addition of the benzoyl chloride, and finally shaken until all the benzoyl chloride has disappeared. After two or three hours, a white, crystalline product separates and floats on the benzene solution, and represents a 72 per cent. yield of the benzoyl derivative, which, after crystallising from alcohol, melts at 149—150°. It is sparingly soluble in ether or benzene, and quite insoluble in dilute acids. On the latter account, the compound must be an imino- and not a hydroxy-derivative, since the basic character of the original substances has evidently been destroyed by the introduction of the benzoyl group.

Reaction with Nitrous Acid.—In this case the two compounds show a remarkable difference of behaviour. Both compounds, when dissolved in cold dilute hydrochloric or acetic acid and treated with potassium nitrite solution, gave precipitates which, after careful washing, gave Liebermann's test for nitroso-compounds. Both compounds would therefore appear to be secondary bases, but there is this difference. In the case of the α -compound the precipitate is a yellow, oily substance, which cannot be obtained crystalline, whilst the β -compound gives at once a faintly yellow-coloured, crystalline precipitate. The latter was recrystallised from ether and light petroleum, and obtained in plates, melting at 112—113°:

0.1100 gave 0.2635 CO_2 and 0.0715 H_2O . $\text{C} = 65.3$; $\text{H} = 7.22$.

$\text{C}_{12}\text{H}_{16}\text{O}_2\text{N}_2$ requires $\text{C} = 65.45$; $\text{H} = 7.27$ per cent.

Action of Methyl Iodide.—The α - and β -compounds react slowly with methyl iodide, forming sometimes a gummy substance, which afterwards becomes crystalline, and sometimes forming a crystalline product directly.

The products were readily soluble in alcohol, and appeared to be mixtures.

The aqueous solutions have an acid reaction, and on treatment with sodium carbonate or sodium hydroxide each compound yielded a small quantity of oily precipitate, which crystallised on keeping; this was readily soluble in ether, but very sparingly so in light petroleum. On repeated crystallisation from a mixture of ether and light petroleum, the products from the α - and β -compounds separated in fine needles, melted at 45—46°, and were apparently identical. It seems probable that this is the methyl derivative, $\text{C}_6\text{H}_3\text{Me}_2\cdot\text{NMe}\cdot\text{CHMe}\cdot\text{CH}_2\cdot\text{CHO}$. This product resembles 2:6:8-trimethylquinoline in some respects, but the solubility in light petroleum discriminates between them, since the quinoline derivative is readily soluble in this solvent.

Other pure compounds have not been separated from the products

of the action with methyl iodide, but on repeated recrystallisation the melting point varied from 215° to 230° , and the composition was apparently that of a mixture. It is probable that in each case the product is a mixture of the methyl iodide additive compounds of 2:6:8-trimethylquinoline and of the tertiary base mentioned above, together with the hydriodide of the latter.

Analogous Compounds from other Amines.—Several amines, including aniline, *o*- and *p*-toluidines, *o*- and *p*-xylydines, and ψ -cumidine, were treated with acetaldehyde in acid solution in the same manner as *m*-4-xylydine. The precipitates obtained by neutralisation in presence of light petroleum varied considerably in appearance. In two cases, those of *p*-toluidine and ψ -cumidine, the precipitate was slightly coloured and crystalline, but the other amines gave products which were viscous and dark coloured. The products obtained from *p*-toluidine and ψ -cumidine were fractionally crystallised, and found to consist of mixtures of two isomerides corresponding with the α - and β -xylydine isomerides, along with compounds corresponding with bimolecular ethylydene-xylydine. In the ψ -cumidine product, the latter derivative predominates, and it is probable that, with many of the other bases, the isomeric pairs of compounds only form a very small part of the product, the regular condensation product being the polymerised Schiff's base.

The β -compound isolated from the *p*-toluidine product consisted of small, colourless plates, melting at 164 — 167° , readily separated from the α -compound by crystallisation:

0.1570 gave 0.4265 CO_2 and 0.1185 H_2O . $\text{C}=74.1$; $\text{H}=8.38$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.57$; $\text{H}=8.47$ per cent.

The α -compound can be obtained by recrystallising the more soluble product and picking out the stout plates, which melt at 108 — 110° :

0.1673 gave 0.4555 CO_2 and 0.1295 H_2O . $\text{C}=74.23$; $\text{H}=8.60$.

$\text{C}_{11}\text{H}_{15}\text{ON}$ requires $\text{C}=74.57$; $\text{H}=8.47$ per cent.

From the cumidine product the derivatives isolated were:

The less soluble β -compound, melting at 110 — 112° :

0.2112 gave 0.5875 CO_2 and 0.0760 H_2O . $\text{C}=75.3$; $\text{H}=9.25$.

$\text{C}_{13}\text{H}_{19}\text{ON}$ requires $\text{C}=76.0$; $\text{H}=9.27$ per cent.

The α -compound melts at 80° .

The bimolecular Schiff's base, soluble in light petroleum, was also isolated, and melted at 160 — 161° . It closely resembles the corresponding xylydine compound in its properties:

0.1727 gave 0.5140 CO_2 and 0.1415 H_2O . $\text{C}=81.2$; $\text{H}=9.4$.

$\text{C}_{22}\text{H}_{30}\text{N}_2$ requires $\text{C}=81.98$; $\text{H}=9.3$ per cent.

These results show that the cause of the isomerism is not in any way connected with the benzene nucleus in *m*-4-xylydine, but is apparently general.

The expenses of this investigation have been defrayed by means of a grant from the Government Grant Committee of the Royal Society, for which we are glad to make this grateful acknowledgment.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

LXIV.—*The Absorption Spectra of p-Toluidine, m-Xylydine, and of their Condensation Products with Acetaldehyde.*

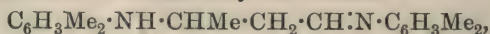
By JOHN EDWARD PURVIS.

WITH regard to the preceding investigations of Jones and White, it appeared to be of some interest to study the absorption spectra of the compounds they obtained in order (1) to compare the spectra with those of *p*-toluidine and of *m*-4-xylydine, and (2) to compare the spectra with each other so as to differentiate, if possible, the suggested linking of the nitrogen atom.

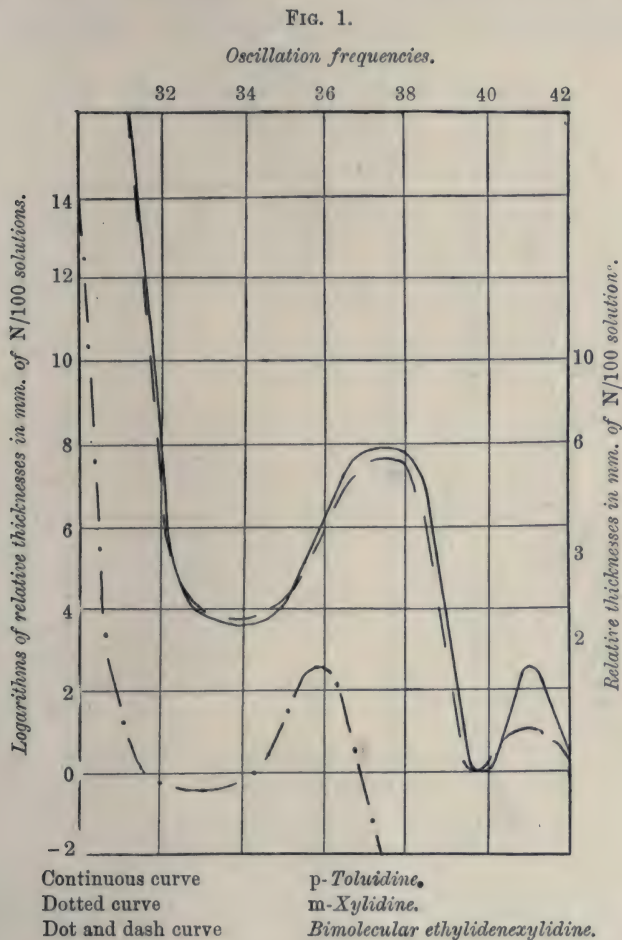
The absorption spectrum of *p*-toluidine has been examined by Hartley (Trans., 1885, **47**, 685), and he found two bands in the dilutions he employed, one range being λ 3171— λ 2701, and the other λ 2568— λ 2310. The absorption curves have been investigated by the method and apparatus used by Purvis and Foster (*Proc. Camb. Phil. Soc.*, 1908, **14**, 381), and the results confirm Hartley's observations. It will be noticed (Fig. 1) that there are two bands, and that before the appearance of the band on the less refrangible side, the one on the more refrangible side of the spectrum disappears as the thickness of the solution increases.

The spectrum of *m*-4-xylydine has not hitherto been studied, and from the absorption curve it will be seen that the bands are similar to those of *p*-toluidine. The differences are that the weighting of the molecule has produced a slight shift of the bands towards the red end of the spectrum, and also that the bands are not quite so persistent, the difference in this respect being greater for the more refrangible band.

The bimolecular ethylenexylydine (m. p. 144—145°), the constitutional formula of which may be written



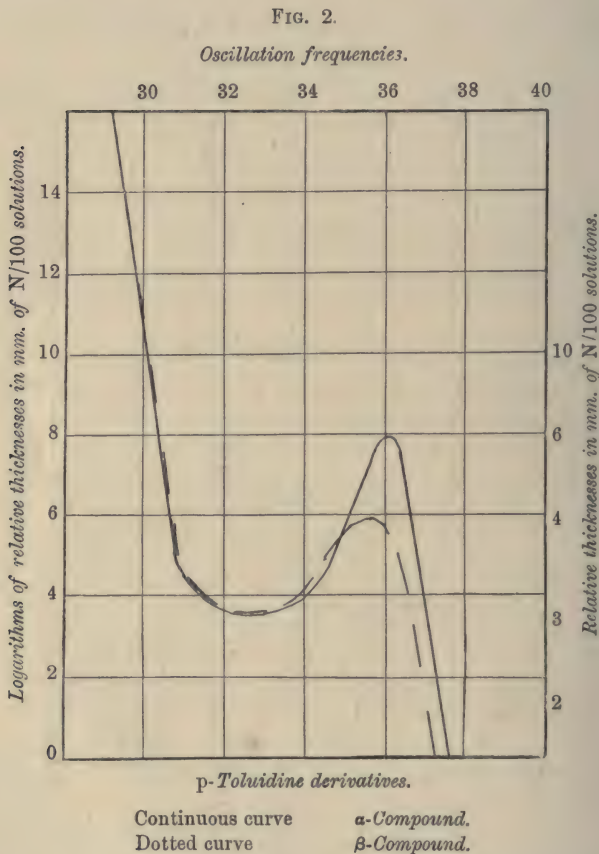
was examined, and from the absorption curve (Fig. 1) it will be noticed that there has been a great shift of the band towards the red end of the spectrum, and that only one band was observed, the persistency of which was considerably diminished. The band on the more refrangible side occurring in *m*-4-xylydine was not



observed; and, although more diluted solutions of $N/1000$ and $N/10,000$ strengths were also examined, there were merely indications of this second band. The effect of the union of the two similar xylydine residues by the aliphatic group has been to reduce the persistency of the bands and not to destroy them.

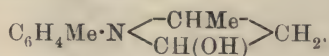
The condensation product of *p*-toluidine and acetaldehyde

(α -form, m. p. 108—110°), $C_6H_4Me \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, was examined; and as regards the general form and persistency, the curve (Fig. 2) shows the presence of only one band, very similar to the band of *p*-toluidine on the less refrangible side of the spectrum. This band is shifted more towards the red end as a result of the



weighting of the molecule, and the second band on the more refrangible side has disappeared.

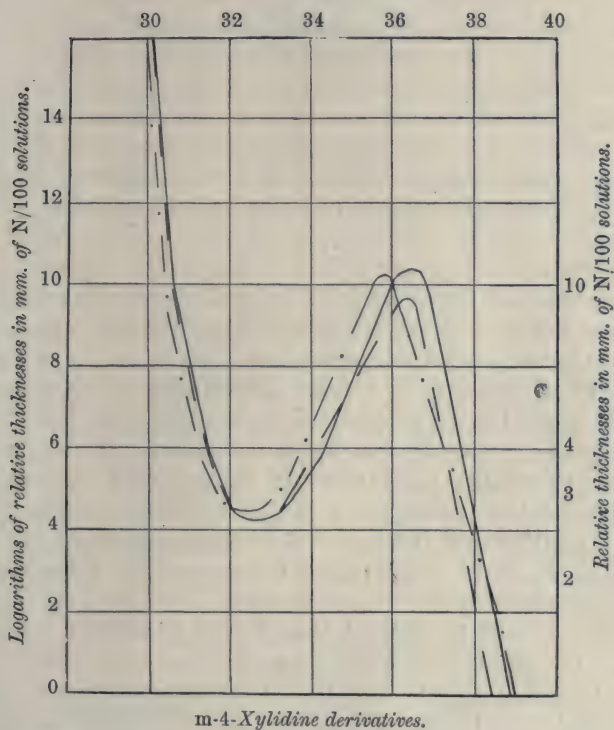
The corresponding β -compound (m. p. 164—167°), the suggested constitutional formula of which is:



was also examined, and it will be noticed that the absorption curve (Fig. 2) is similar to that of the α -isomeride both in form and position, although it is slightly less persistent.

The condensation product of *m*-4-xylidine and acetaldehyde (α -form, m. p. 103—104°), $C_6H_3Me_2 \cdot NH \cdot CHMe \cdot CH_2 \cdot CHO$, was examined, and on comparing the curve (Fig. 3) with that of *m*-4-xylidine, it is noticeable that only one band is visible, the persistency of which is greater than that of the latter substance, and also greater than that of the corresponding compound obtained from *p*-toluidine. The band on the more refrangible side has

FIG. 3.

Oscillation frequencies.

Continuous curve	α -Compound.
Dotted curve	β -Compound.
Dot and dash curve	α -Compound with hydrochloric acid.

disappeared, exactly similar to the effect in the corresponding substance obtained from *p*-toluidine.

The β -compound (m. p. 127—128°), the constitutional formula of which, it is suggested, may be:



was examined, and the absorption curve (Fig. 3) is not unlike that of the α -compound, although it is not quite so persistent. There is therefore precisely the same kind of difference between these two substances as between the two corresponding substances obtained from *p*-toluidine.

It has been noticed by Hartley (*loc. cit.*), Baker and Baly (Trans., 1907, **91**, 1122), and Purvis (*Proc. Camb. Phil. Soc.*, 1908, **14**, 436) that the effect of adding hydrochloric acid to the bases, pyridine, lutidine, and trimethylpyridine respectively was to produce a marked increase in the persistence of the absorption curves. The author has also shown (*Proc. Camb. Phil. Soc.*, 1908, **14**, 568) that in tetrachloro-2-aminopyridine and tetrachloro-4-aminopyridine the absorption curves differ widely in their positions and persistencies, the orientation of the amino-group determining the nature and extent of the absorption; and, further, that the substitution of atoms forming part of a side-chain does not exert the same marked influence on the absorption of light as when the substitution takes place in the nucleus (Trans., 1909, **95**, 294).

In order to test how far the vibrations of the aromatic ring of the compounds of the present investigation are affected when the nitrogen atom is part of a side-chain, the absorption curve was studied when hydrochloric acid was added to the α -compound (m. p. 103—104°) obtained from *m*-4-xylydine. The results show (Fig. 3) that the form and persistency of the curve are not different from those of the latter compound. There is only a greater shift of the band towards the red end, caused by the weighting of the molecule by the acid. They confirm the view that the position and linking of the nitrogen atom in the ring or the side-chain is of considerable importance in determining the absorption of light.

Further, it will be noticed that in the bimolecular ethylidene-xylydine the linking of the nitrogen atom of the two xylydine groups is different. On one side it is linked with two atoms of carbon and an atom of hydrogen; and on the other side it is linked with two atoms of carbon. In the latter case the linking of the nitrogen atom with a carbon atom of the aliphatic residue is a double one. The effect has been to reduce the absorption, and therefore the persistencies of the bands, although the general form of the curve has been retained.

The effect of the nitrogen linking in the α -compound obtained from *p*-toluidine has been to obliterate the more refrangible band, whilst the less refrangible one remains very similar to that of the parent substance both in form and persistency. The curve obtained

from the β -compound is also very similar, the only difference being that it is not so persistent. This difference probably indicates some alteration in the linking of the nitrogen atom, which may be in the direction of the suggested formula.

As regards the α - and β -compounds obtained from *m*-4-xyldine, which correspond with the α - and β -compounds obtained from *p*-toluidine, similar remarks apply, for the persistence of the curve of the β -compound is not so marked as that of the α -compound. The phenomena observed in the two series of compounds are precisely similar in this respect; and the linking of the nitrogen atom appears to be exactly the same.

It is not clear, however, how far these results assist the suggested formulæ of the β -compounds. We might have expected a somewhat different form of curve in compounds containing two rings of such different types. At the same time, there can be little doubt that the nitrogen atom is a determining factor in the absorption, and the suggestion that it is linked to three separate carbon atoms in these compounds, whereas in the isomerides it is linked to two carbon atoms, derives some support from the different persistencies of the bands. In such linkings the tendency would be to influence the vibrations so that less light would be absorbed, and it would be manifested in a decreased persistence of the absorption band. It is also conceivable that the vibrations of the aromatic ring are more fundamentally influenced by the combination with the nitrogen atom than are those of the aliphatic ring; or, in other words, if the aliphatic parts of the compounds are considered as displacing the hydrogen atoms of the amino-groups, the small differences shown by the curves may be explained by the previous observations that there is less influence on the vibrations of the nucleus in such a case than when the displacement takes place in the nucleus itself (Trans., 1909, 95, 294).

General Results.

The general results of the investigation show:

1. That the absorption curves of *p*-toluidine and *m*-4-xyldine are very similar. The chief differences are the slightly decreased persistence of the bands of *m*-4-xyldine, and the shifting of the bands of the heavier molecule towards the red end of the spectrum.
2. That the combination of two *m*-4-xyldine residues through acetaldehyde produces a greatly decreased persistence of the two bands and also a greater shift towards the red end.
3. That the isomeric substances obtained by the union of *p*-toluidine or of *m*-4-xyldine with acetaldehyde produce a disappearance of the more refrangible band found in the aromatic

compounds; and that the isomeric substances show differences in the persistence of the remaining band, the origin of which may be explained from a consideration of differences in the nitrogen linking.

4. That the addition of hydrochloric acid to these derived compounds has no effect on the form and persistence of the absorption band, thereby indicating that the vibrations of the nucleus are not influenced by an alteration in the valency of the nitrogen of the side-chain.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

ANNUAL GENERAL MEETING,

MARCH 18TH, 1910.

Prof. HAROLD B. DIXON, M.A., Ph.D., F.R.S., in the Chair.

Mr. J. S. S. BRAME and Dr. N. V. SIDGWICK were appointed Scrutators, and the ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society during the past twelve months was presented by the PRESIDENT, and the Treasurer, after making a statement as to the Society's income and expenditure for 1909, proposed a vote of thanks to the Auditors, which was seconded by Mr. A. C. CHAPMAN and acknowledged by Dr. J. A. VOELCKER.

The adoption of the Report of Council together with the Balance Sheet and Statements of Accounts for the year ended December 31st, 1909, proposed by Dr. G. MCGOWAN and seconded by Dr. H. BRERETON BAKER, was put to the Meeting and carried unanimously.

REPORT OF THE COUNCIL.

The Council is again in a position to report favourably on the progress of the Society, as indicated by an increase in the number of Fellows and in the list of papers communicated.

On the 31st December, 1908, the number of Fellows was 2,950. During 1909, 160 Fellows have been elected and 7 were reinstated, the gross total thus being 3,117. The Society has lost 25 Fellows by death; 43 have resigned; the election of 2 Fellows has become void, and 44 Fellows have had their names removed from the List for non-payment of Annual Subscriptions.

The total number of Fellows, therefore, at the 31st December, 1909, was 3,003, showing a net increase of 53 over the preceding year.

The names of the deceased Fellows, with the dates of their election, are :

R. Bannister (1871).	F. Norton (1854).
J. Castell-Evans (1903).	G. E. Perry (1888).
E. J. Cox (1886).	E. A. Pontifex (1848).
C. B. Dudley (1898).	T. H. Redwood (1887).
C. Ekin (1864).	W. B. Roberts (1880).
J. Fuller (1886).	W. J. Russell (1851).
C. Graham (1862).	W. Stewart (1872).
H. E. Harrison (1883).	F. Stocks (1874).
W. H. Hudleston (1871).	C. Thomas (1871).
S. H. Johnson (1866).	H. E. Thomas (1874).
J. J. Kielty (1903).	Sir T. Wardle (1875).
L. Mond (1872).	A. F. Watson (1893).
J. H. Wilson (1878).	

The following Fellows have resigned

E. W. Bealey.	C. P. Hines.	J. M. Murray.
H. J. Brown.	E. Houghton.	P. G. Pennymore
T. S. Busher.	A. Howard.	H. Richardson.
E. Catherall.	R. S. Hutton.	H. E. Richardson.
E. Cleminshaw.	A. J. Hyder.	J. Richardson.
A. J. Cook.	A. James.	*C. J. Smith.
J. W. Daniels.	W. H. M. Jones.	T. Southern.
J. H. Davidson.	J. Leicester.	W. S. Templeton.
F. R. Dudderidge.	A. G. Levy.	R. Tervet.
E. J. Fairhall.	R. D. MacKechnie.	A. Tighe.
C. Gordon.	W. Mackean.	S. Tolson.
J. H. Gough.	A. McMullen.	A. J. Webb.
H. W. Harrie.	C. A. MacMunn.	G. H. West.
J. W. Helps.	*C. Müller.	F. G. Wiechmann.

and Professor Dr. Georg Lunge, whose name has been transferred from the list of Fellows to that of the Honorary and Foreign Members.

The number of those Fellows elected previous to the year 1860 has been diminished still further by the death of Mr. Fletcher Norton, elected on December 18th, 1854, of Mr. Edmund Alfred Pontifex, elected December 4th, 1848, and of our distinguished Past-President, Dr. William James Russell, F.R.S., elected March 3rd, 1851.

The number of Honorary and Foreign Members at the close of 1909 was 34. One election has taken place, and the Society has to mourn the loss of Professor Emil Erlenmeyer, and of Professor Julius

* Included among the seven reinstated Fellows.

Thomsen, who passed away early last year, making the total number of Honorary and Foreign Members at December 31st, 1909, amount to 33.

The Council has much pleasure in congratulating the following gentlemen, who, during the past year, have reached their Jubilee as Fellows of the Society:

Prof. Dr. Heinrich Debus, F.R.S.
 Mr. Thomas Fogg.
 Dr. A. G. Vernon Harcourt, F.R.S.
 Mr. Josiah W. Kynaston.
 Dr. Hugo Müller, F.R.S.
 Mr. Thomas W. Salter.
 Mr. John Spiller.

During the year 1909, 300 scientific communications have been made to the Society, 227 of which have been published already in the Transactions, and abstracts of all have appeared in the Proceedings.

The volume of Transactions for 1909 contains 2,219 pages, of which 2,133 are occupied by 236 memoirs, the remaining 86 pages being devoted to the Obituary Notices, the Wolcott Gibbs and Mendeléeff Memorial Lectures, the Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 222 memoirs, which occupy 2,188 pages.

The Journal for 1909 contains 4,946 abstracts, which extend to 2,040 pages, whilst the abstracts for 1908 numbered 4,978, and occupied 2,112 pages. The abstracts for 1909 may be classified as follows:

PART I.

	Pages.	No. of Abstracts
Organic Chemistry.....	980	1,781

PART II.

General and Physical Chemistry		953
Inorganic Chemistry		565
Mineralogical Chemistry		144
Physiological Chemistry		577
Chemistry of Vegetable Physiology and Agriculture.....		304
Analytical Chemistry		622
	1,060	3,165
Total in Parts I. and II.	2,040	4,946

Since the last Annual General Meeting, three Memorial Lectures, dealing with the life-work of deceased Honorary and Foreign Members have been delivered. On the 3rd of June, 1909, Dr. Frank Wigglesworth Clarke paid this tribute to the late Professor Wolcott Gibbs; Sir William Tilden delivered the Mendeléeff Memorial Lecture on October 21st, and Sir Edward Thorpe reviewed the thermochemical and other researches of Professor Julius Thomsen in a discourse given before the Society on February 17th, 1910.

The year 1911 marking the hundredth anniversary of Avogadro's celebrated memoir, the Council has voted a contribution of £10 from the funds of the Society towards the international commemoration of the event. Fellows have been invited also to participate in the celebration of Professor Körner's seventieth birthday, which will be recognised on behalf of the Society by the presentation of an illuminated address of congratulation in May next.

The rapid growth of the Library since the contents of the rooms at Burlington House were valued, has necessitated the preparation of a fresh estimate of replacement cost; this has now been completed, and an arrangement based thereon will be concluded with the Insurance Company.

During the past year the Chemical Society has become indebted to the Society of Dyers and Colourists for the gift of a reproduction in bronze of the plaque by Mr. F. W. Pomeroy, R.A., representing the late Sir William Perkin. Professor Meldola has added to the collection of photographs an interesting one of the Jury (Paris Exhibition, 1900), which included among its members the late Professor Mendeléeff, and the Society has also received valuable gifts of books from Mrs. J. Wilson, Mr. A. Gamble, and Mr. F. Stocks.

In chronological order, Past-Presidents the Rt. Hon. Sir Henry Roscoe, Sir William Crookes, Dr. Hugo Müller, and Dr. A. G. Vernon Harcourt have more than completed fifty years of Fellowship, whilst Professor William Odling, who has now been for sixty-two years a Fellow, and became President in 1873, is the sole survivor of the six Past-Presidents who were entertained to a banquet in 1898. Desiring to do honour to these gentlemen in the name of the Society, the Council, through the President, has invited them to a banquet to be held during the ensuing summer, believing that a considerable number of Fellows will be glad to assist at this interesting commemoration, details of which will be announced forthwith.

With the object of meeting a widely expressed desire, the Report of the International Committee on Atomic Weights will in future, it is hoped, be published in September instead of in January. This will render it immediately useful to College teachers at the beginning of each new Session. In order to adapt the list of amended Atomic

Weights to the requirements of students, it is now printed on paper as well as on cardboard.

The Council desires to place on record its high appreciation of the valuable services rendered to the Society by Dr. M. O. Forster, who now retires from the position of Honorary Secretary, which he has held for the last six years. Dr. Forster has given unsparingly both his time and his energy to the work of the Society, and has ever been active in promoting its highest interests.

The number of books borrowed from the Library during the year 1909 was 1,548, as against 1,339 in the previous year; of these, 347 were issued by post, as against 338 in the preceding year.

The additions to the Library comprise: 142 books, of which 72 were presented, 418 volumes of periodicals (representing 243 journals), and 80 pamphlets, as against 159 books, 412 volumes of periodicals (representing 245 journals), and 36 pamphlets last year.

The income of the Society for the year shows an increase of £252 10s. 10d. over that of last year, the amounts being £7,387 8s. and £7,134 17s. 2d. respectively, whilst the expenditure has risen from £6,834 15s. to £7,028 3s. 5d. This leaves in the Treasurer's hands a balance of £359 4s. 7d. on the year's working, which together with the balance of £300 saved in 1908 has enabled the Council to authorise the purchase of £700 Canadian 3½ per cent. stock.

In the balance-sheet for this year there appears for the first time a valuation of the Library, Furniture, Bronzes, Busts, &c. This has been based on a complete inventory which has now been made in order to be used as the basis for the new Fire Insurance Policy which will be arranged in June next, when the present policy expires.

Thanks to the care of the Publication Committee and the Editor, the net cost of the annual publications (taking account of their increased sales) only shows a rise of about £25, and this, be it noted, includes the preparation for the next volume of the Decennial Indexes which is now fairly under way. The cost of indexing no longer appears as a separate item in our accounts, as it has been entirely taken over by the Editor and is included in his salary. There has been a reduction of nearly £100 in the cost of the Annual Reports, whilst house expenses and repairs cost about £50 less than last year. The chief items in the expenditure which are not of annual occurrence are the new cases for the Library costing £93 10s., and the balance of the Dinner account, which was no less than £70 9s. 6d.

From the Research Fund grants were made amounting in all to £369, and as this year there was the further outlay on the Longstaff Medal and its accompanying Honorarium, the expenditure exceeded the income by £34 17s. 1d., this deficit being met from the balance in hand. During the last six years grants have been

INCOME AND EXPENDITURE ACCOUNT

		<i>Income.</i>			
		£	s. d.	£	s. d.
To Life Compositions				287	0 0
„ Admission Fees				628	0 0
„ Annual Subscriptions—					
Received in advance, on account of 1909		255	0 0		
„ during 1909	1909	4132	0 0		
„ „ „ „ 1908	1908	360	0 0		
„ „ „ „ 1907	1907	10	0 0		
		4757	0 0		
Less amount included in last year's Income, being valuation of Arrears as per last Balance Sheet		340	0 0		
		4427	0 0		
Add Arrears at date: 1909 £442; 1908 £20; 1907 £2, estimated to realise as per Balance Sheet		356	0 0		
				4783	0 0
„ Lady Subscribers				3	0 0
„ Investments:—					
Dividends on £6730 Metropolitan Consolidated 3½ per cent. Stock ...		222	16 0		
„ £1050 London and North Western Railway 3 per cent. Debenture Stock		29	17 2		
„ £1520 14s. 3d. Cardiff Corporation 3 per cent. Stock ...		43	3 1		
„ £1400 India 2½ per cent. Stock		33	2 2		
„ £2400 Bristol Corporation 2½ per cent. Debenture Stock ...		56	15 0		
„ £4341 Midland Railway 2½ per cent. Preference Stock ...		102	17 6		
„ £1200 Leeds Corporation 3 per cent. Stock		34	1 0		
„ £1500 Transvaal 3 per cent. Guaranteed Stock		42	7 6		
„ £1200 North British Railway 3 per cent. Debenture Stock		34	0 4		
„ Income Tax Recovered		31	13 0		
„ Interest on Deposit Account		13	5 11		
				643	18 8
„ Publications:—					
Sales:					
Journals		880	9 11		
Proceedings		36	11 11		
General Index		13	5 0		
Memorial Lectures		3	17 7		
Library Catalogue		1	9 3		
Atomic Weight Tables		17	7		
Annual Reports on the Progress of Chemistry		139	4 6		
		1075	15 9		
Less Publishers' Commission		103	3 5		
		972	12 4		
Proceeds of Advertisements in Journal	£42 18 3				
Less Commission	6 8 9				
		36	9 6		
				1009	1 10
„ Sale of Royal Society Proceedings				3	3 0
„ Sale of Waste Paper				9	15 0
„ Subscriptions from other Societies:—					
Society of Chemical Industry		8	8 0		
Society of Public Analysts		12	1 6		
				20	9 6
				£7387	8 0

I have examined the above Accounts with the Books and Vouchers of the Society, and the Investments.

FOR THE YEAR ENDED 31ST DECEMBER, 1909.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings:—						
Salary of Editor, including Indexing	545	15	0			
Salary of Sub-Editor	200	0	0			
Editorial Postages	22	13	2			
Abstractors' Fees	435	18	8			
Printing of Journal	2588	0	9			
Illustrations... ..	19	8	11			
Banding	57	7	8			
Printing of Advertisements	26	12	0			
Wrappers and Addressing	118	13	6			
Distribution of Journal	536	18	1			
Authors' Copies	174	12	6			
Insurance of Stock at Clay's	7	0	0			
				4778	0	3
Printing of Proceedings	208	4	6			
Banding „	11	2	4			
Distribution „	42	11	4			
				261	18	2
„ Annual Reports on the Progress of Chemistry				421	14	2
„ Purchase of back numbers of Journal				8	18	3
„ List of Fellows				64	4	6
„ Library Expenses:—						
Salary of Librarian and Assistant... ..	144	8	0			
Books and Periodicals	240	8	11			
Binding	44	11	7			
New Bookcases	93	10	0			
				522	18	6
„ Indexing for International Catalogue				30	0	0
„ Subscription to Avogadro Memorial				10	0	0
„ Balance of Dinner Account				70	9	6
„ Administrative Expenses:—						
Salary of Assistant Secretary	260	0	0			
Salary of Office Assistant... ..	36	0	0			
Wages (Commissionaire, Housekeeper, and Charwoman)	160	2	6			
Pension, Mrs. Hall	30	0	0			
Coal and Lighting	35	12	10			
House Expenses and Repairs	55	17	9			
Tea Expenses	27	2	10			
Insurances	9	15	2			
Accountants' Charges, balance for 1908	5	5	0			
„ „ „ 1909	21	0	0			
Commission on Recovery of Income Tax	1	11	8			
Honorarium for Valuation of Library	25	0	0			
Printing	76	16	1			
Stationery	16	13	8			
Postages	75	6	0			
Furniture	5	11	6			
Miscellaneous Expenses	18	5	1			
				860	0	1
„ Balance, being excess of Income over Expenditure, carried to Balance Sheet				359	4	7

£7387 8 0

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved—

J. AUGUSTUS VOELCKER,
VICTOR H. VELEY,
FREDERICK B. POWER,

Liabilities.

	£	s.	d.
To Subscriptions received in advance	275	0	0
" Cash received on Account of Annual Report, Vol. VI. (not published)	27	10	6
" Sundry Creditors	1130	14	0
" Research Fund:—			
As per last Balance Sheet	10510	12	5
Less Excess of Expenditure over Income for the year	34	17	1
	10475	15	4
Chemical Society: Excess of Assets over Liabilities:—			
As per last Balance Sheet	10945	11	10
Add Excess of Income over Expenditure for the year	859	4	7
	20804	16	5

£32213 16 3

Assets.

	£	s.	d.
By Investments (value when acquired):—			
£6730 Metropolitan Consolidated 9½ per cent. Stock	7212	8	6
£1050 London and North Western Railway 3 per cent. Debenture Stock	830	12	0
£1520 14s. 3d. Cardiff Corporation 3 per cent. Stock	1650	0	0
£1400 India 2½ per cent. Stock	1816	1	0
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070	2	0
£4341 Midland Railway 2½ per cent. Preference Stock	3572	2	5
£1200 Leeds Corporation 3 per cent. Stock	1143	1	0
£1500 Transvaal 3 per cent. Guaranteed Stock	1460	13	6
£1200 North British Railway 3 per cent. Debenture Stock	1033	11	0
	20297	11	5
(Estimated present value of Investments,			
£18177 13s. 11d.)			
" Sundry Debtors:—			
Society of Public Analysts	12	1	6
Advertising Agents	36	9	6
Messrs. Gurney & Jackson	434	1	6
Telephone Deposit	1	0	0
" Subscriptions in Arrear, £464. Estimated to realise	483	12	6
" Insurance paid in advance	356	0	0
" Cash at Bank:—			
Deposit Account	560	0	0
Current Account	93	12	3
Cash in hand	3	16	4
" Research Fund:—			
Investments (value when acquired):			
£1000 North British Railway 4 per cent. No. 1 Preference Stock	1010	0	0
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587	18	0
£21034 Great Western Railway 2½ per cent. Debenture Stock	1049	15	11
£21142 10s. New South Wales 3 per cent. Stock	1000	0	0
£1122 Metropolitan Water Board 3 per cent. "B" Stock	1002	16	9
£1365 Midland Railway 2½ per cent. Debenture Stock	1010	0	0
£803 Victoria 3 per cent. Stock	706	6	2
	10363	17	7
(Estimated present value of Research Fund Investments, £9899 16s. 8d.)			
" Cash at Bank	108	17	9
	10475	15	4

483 12 6

356 0 0

8 8 5

597 8 7

NOTE.—The estimated value of the Library, exclusive of the Stock of the Society's own publications, is £7200, and of the Furniture &c., £3350.

£32213 16 3

made to 183 out of 216 applicants, the total amount applied for having been £2,845, of which £1,673 was granted, and of this £57 has been refunded. In return, 160 papers have appeared in our Transactions, 18 in the Proceedings, and 22 in other journals.

A vote of thanks to the Treasurer, Honorary Secretaries, Foreign Secretary, and Council for their service during the past year was proposed by Dr. BERNARD DYER, seconded by Mr. E. GRANT HOOPER, and acknowledged by Dr. M. O. FORSTER, the retiring Hon. Secretary.

The PRESIDENT then delivered his address, entitled "The Union of Hydrogen and Oxygen in Flame." Dr. A. G. VERNON HARCOURT proposed a vote of thanks to the President coupled with the request that he would allow his address to be printed in the Transactions. The motion was seconded by Sir EDWARD THORPE and carried with acclamation, and acknowledged by the PRESIDENT.

The Scrutators having presented their report, the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year :

President : Harold B. Dixon, M.A., F.R.S.

Vice-Presidents who have filled the Office of President : H. E. Armstrong, Ph.D., LL.D., F.R.S. ; A. Crum Brown, D.Sc., LL.D., F.R.S. ; Sir William Crookes, D.Sc., F.R.S. ; Sir James Dewar, M.A., LL.D., F.R.S. ; A. Vernon Harcourt, M.A., D.C.L., F.R.S. ; Raphael Meldola, F.R.S. ; H. Müller, Ph.D., LL.D., F.R.S. ; W. Odling, M.A., M.B., F.R.S. ; Sir William Ramsay, K.C.B., LL.D., F.R.S. ; J. Emerson Reynolds, Sc.D., M.D., F.R.S. ; The Rt. Hon Sir Henry E. Roscoe, LL.D., F.R.S. ; Sir Edward Thorpe, C.B., LL.D., F.R.S. ; Sir William A. Tilden, D.Sc., F.R.S.

Vice-Presidents : J. Norman Collie, Ph.D., F.R.S. ; J. J. Dobbie, M.A., D.Sc., F.R.S. ; M. O. Forster, D.Sc., Ph.D., F.R.S. ; F. Stanley Kipping, D.Sc., Ph.D., F.R.S. ; A. Liversidge, LL.D., F.R.S. ; J. Walker, D.Sc., Ph.D., F.R.S.

Treasurer : Alexander Scott, M.A., D.Sc., F.R.S.

Secretaries : A. W. Crossley, D.Sc., Ph.D., F.R.S. ; G. T. Morgan, D.Sc.

Foreign Secretary : Horace T. Brown, LL.D., F.R.S.

Ordinary Members of Council : Julian L. Baker ; George T. Beilby, F.R.S. ; William A. Bone, D.Sc., Ph.D., F.R.S. ; Adrian J. Brown, M.Sc. ; Julius B. Cohen, Ph.D., B.Sc. ; Charles E. Groves, F.R.S. ; J. T. Hewitt, M.A., D.Sc., Ph.D. ; H. R. Le Sueur, D.Sc. ; Alex. McKenzie, D.Sc., Ph.D. ; J. C. Philip, D.Sc., Ph.D. ; Sir Boverton Redwood, D.Sc. ; A. E. H. Tutton, M.A., D.Sc., F.R.S.

PRESIDENTIAL ADDRESS.

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By HAROLD B. DIXON, M.A., Ph.D., F.R.S.

The Union of Hydrogen and Oxygen in Flame.

IN his presidential address last year, my distinguished predecessor in this Chair quoted with approval that clever definition which distinguishes a theory from a hypothesis—"a theory is a supposition we hope to be true; a hypothesis is a supposition we expect to be useful." I do not know whether the majority of scientific people hope that the theories they employ are true; I feel very sure they become convinced of their truth by a long habit of using them. Suppositions that have stood the criticism of Time, and have been *taught to us as accepted theories*, take possession of our minds whether we will or no. I have heard St. Claire Deville, who professed his disbelief in *all* theories, lapse unconsciously into the atomic theory in moments of controversy. Such theories become almost an essential part of our mental apparatus, and perhaps no great harm results if the majority of us believe in them as an article of scientific faith. The danger lies in the hypothesis "we expect to be useful." In its inception it is a more or less plausible guess—often arrived at by analogy. We try it (with proper scepticism) to see if it will "work." If it serves we try it again with less mental reserve. The hypothesis suggests certain consequences under certain conditions; if we find these consequences follow in a few trials we are apt to regard our hypothesis as "verified," and we begin to think in terms of it—especially if we have published it. By and by our hypothesis becomes crystallised in our system, and if further consequences are not in accord with it, we—to reform the language of the unreformed Chamber—*disregard* the consequences. But the hypothesis, however useful it may be as a means of winning new facts, or new views of facts, is by no means proved to be true by successful prediction. We must be continually on our guard lest we become the bondmen of our own hypotheses, although I do not think that we Britons, as a race, are the worst offenders. "Chemists," wrote Stas, "the instant they see certain facts are reproduced with an *appearance* of regularity, believe this is a simple natural law; moreover, they have contracted the habit of considering that the law has been demonstrated the moment they have made any measurements not greatly differing from it."

I am not claiming for myself exemption from the common infirmity. I have made hypotheses, and very possibly have allowed them to bias my judgment. Moreover, I have suffered what Huxley called that great tragedy of science—"the slaying of a beautiful hypothesis by an ugly fact." But I regard this as a proper and desirable ending, and am glad to have helped in the "happy dispatch," not only of my own, but of those of some of my fellow-workers.

I would urge, then, that it is the present *usefulness* of the hypothesis, not its truth, that is important: we ought to value it only so long as it is a *working* hypothesis, that is, is guiding and suggesting work in the laboratory. We ought, indeed, to do unto our hypotheses as we would do unto professors—other professors—in an ideal university. The moment the hypothesis ceased to work in the laboratory it should be quietly superseded.

My text might have been illustrated from almost any branch of chemistry; I have chosen the union of hydrogen and oxygen in flame, partly because I am more familiar with this subject, and partly because the reactions involved are comparatively simple. It was mainly with the hope of finding, among these or other gases, reactions simple enough to be interpreted and to throw light "on the course of a chemical change," that I started these researches under the guidance of Mr. Vernon Harcourt more than thirty years ago. Though I have, no doubt, wasted much time, I have never regretted the choice of subject, and have never been tempted to turn aside.

The Direct Union of Hydrogen and Oxygen.

I first studied the union of hydrogen and oxygen in flame as part of the investigation on the mode of burning of carbon monoxide. When steam, either present to start with or formed in the flame, was found to be necessary for the propagation of a flame in carbon monoxide-oxygen mixtures, I ventured on my first hypothesis—I think a moderate one. If there is some constitutional disability preventing oxygen from direct combination with carbon monoxide, may not the latter take oxygen from steam, and the hydrogen, so liberated, re-form steam by direct union with oxygen.

I need not at this point discuss what special disability prevents the oxygen from burning the carbon monoxide directly. Many hypotheses have been made to account for it, for example, that the oxygen, *per se*, is too stable (Lothar Meyer, Beketoff), or that gases only react in equal volumes (Mendeléeff). With the aid of several of my old students I have shown, in communications to this Society, that neither the stability of the oxygen, nor the "law of equal

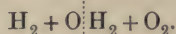
molecules," can be the cause, for carbon monoxide will not explode with ozone, with chlorine monoxide, or with nitrous oxide. On the other hand, the dried gases unite readily *without inflaming* in the presence of red-hot platinum, and in the burning of dried cyanogen the carbon monoxide first formed will burn in excess of oxygen—either prolonging the flame, as in explosions, or burning with a separate flame, as in the Smithells' flame-separator. Steam, then, is necessary for the burning of carbon monoxide only *under certain conditions*. How does it act? Carbon monoxide was found to take oxygen from steam and liberate the hydrogen when the two were heated together in a variety of ways. In explosion of mixtures of carbon monoxide, oxygen, and steam, in which the oxygen was insufficient for complete combustion, the steam was found to give up its oxygen to burn the excess of monoxide. Moreover, the propagation of the flame through the mixture was found to increase in velocity the more steam was added up to 6 per cent. of the mixture. It was therefore possible for the carbon monoxide to take oxygen from steam in a flame, and if the liberated hydrogen united directly with oxygen, water would be re-formed, and the whole operation be completed by the repetition of some simple cycle.

So the next point to investigate was—Does hydrogen unite directly with oxygen in a flame, or does it only do so through the decomposition of or by the intervention of water?

My first experiments on the union of hydrogen and oxygen were high temperature experiments. I found that an electric spark, which would fire a damp mixture of hydrogen and oxygen, would also fire a similar mixture however carefully dried. Many different electrodes were tried, and they were submitted to every process I could devise to prevent the possibility of steam being formed in or on the surface of the electrode. The spark always determined explosion. Moreover, I have analysed (on a rapidly-moving film) the flame of an explosion in electrolytic gas from its starting point at the spark as it spreads into the unburnt gas. The experiments were made in exactly similar tubes, all other conditions being the same—except that, in each pair, one tube was well dried and the other was moist. In no case could any difference be detected between the dried and moist gases either in the initiation or the spread of the flame. Dr. Brereton Baker, than whom I could cite no more careful or patient experimenter, has come to the same conclusion. But it may be objected: "*Some steam molecule may exist in the path of the spark, and that starts the reaction; once started, the water formed serves to spread the flame.*" We cannot, of course, prove that no steam molecules exist in the dried gas—indeed, I

should say it was very probable that there are some. But we have some evidence as to the *progress* of the reaction in the explosion of hydrogen and oxygen, and that evidence we can use to test the point whether the flame, once started, is propagated by direct union of hydrogen and oxygen molecules, or whether that union only takes place through the intervention of a steam molecule.

Both Moritz Traube and Professor Armstrong have put forward the view (on different grounds) that for the formation of steam there must be a simultaneous reaction between three molecules:



Now, the "explosion-wave" is a true physico-chemical constant. The genius of Berthelot was not at fault when he described the advancing locus of high pressure and of rapid chemical change as *l'onde explosive*. The "wave" was propagated, according to Berthelot, from layer to layer by successive shocks between the molecules, resulting in chemical action; so that the explosion-wave differed from a sound-wave in that the former varied, not only with the physical, but with the chemical nature of the gaseous mixture. The maximum velocity of the explosion-wave could be predicted, said Berthelot, by calculating the mean velocity of the gaseous products before they had lost by conduction or radiation any of the heat of the chemical change. My own work on the explosion-wave began in an attempt to confirm or disprove my hypothesis that steam was the "carrier" of oxygen in the explosion of carbon monoxide and oxygen. The results obtained led me to use the explosion-wave as a means of tracing the course of other changes in gases. For instance, it was found most useful in showing that the carbon in gaseous compounds of carbon was not burnt directly to carbon dioxide in explosions, but, in every instance that could be traced, the carbon dioxide, appearing as an end-product, had been produced by a secondary and not by a primary reaction in the wave-front. After many experiments on the diluting effect of various gases on the propagation of the explosion-wave, I was led to advance a "working hypothesis" somewhat different from that of Berthelot. In my hypothesis the gases are not burnt "cold," but the unburnt molecules are heated in the wave-front by "shock," and so are burnt "hot," and consequently the product is raised to a higher temperature. A formula based on this hypothesis was successful in predicting the velocities of the explosion-wave in a number of different gases:

Gas mixture.	Velocity of explosion-wave.	
	Calculated.	Found.
$8\text{H}_2 + \text{O}_2$	3554	3535
$\text{H}_2 + 3\text{O}_2$	1740	1712
$2\text{H}_2 + \text{Cl}_2$	1832	1849
$\text{C}_2\text{N}_2 + \text{O}_2$	2725	2728
$\text{C}_2\text{N}_2 + \text{O}_2 + 2\text{N}_2$	2166	2163
$\text{C}_2\text{H}_4 + 2\text{O}_2 + 8\text{N}_2$	1727	1734

I find it very hard to believe that these extremely close approximations can be mere coincidences.

There are probably many cases in which the reactions are not so simple as the above. I find that the explosion-wave in a mixture of equal volumes of ethane and oxygen does not give the same products as are obtained in the explosion of ethylene, or of acetylene, with its own volume of oxygen. The ethane is not burnt wholly to carbon monoxide and hydrogen, but appears to form (as Professor Bone has shown at lower temperatures) acetaldehyde and steam, the acetaldehyde yielding methane and carbon monoxide.

For other gaseous mixtures, especially those in which steam is formed at a very high temperature, the formula gives a higher value than the rate found. For instance, the found velocity of the explosion-wave in electrolytic gas is a long way below that given by the formula. I "explained" that by the further supposition that the dissociation of steam was appreciable in the explosion-wave of electrolytic gas. In support of this view, I showed that about 1 per cent. of unburnt gas * remained behind after the explosion-wave had gone by, and proved that this could not be attributed to the cooling effect of the walls.

I do not believe to-day in the truth of my working hypothesis of the explosion-wave. It embodied a number of assumptions, some of which I have myself shown to be erroneous. But I still think it was sufficiently parallel to the truth to be useful: I made no higher claim for it.

The theory of the explosion-wave is not to-day dependent on the hypotheses of Berthelot and myself. Sufficient experimental data were secured to allow a mathematical treatment of the subject. Professor Schuster was the first to suggest that Riemann's equation for the propagation of an abrupt variation in the density and pressure of a gas might be applied to the propagation of the explosion-wave, since the necessary uniformity of type is maintained owing to the continued reinforcement of the wave by the successive chemical changes. In 1899 Mr. D. L. Chapman, acting on this suggestion, worked out from Riemann's equation an expression for

* *Mem. Manchester Phil. Soc.*, 1888. The fact was rediscovered in 1897 by F. Emich (*Monatsh.*, 18, 6), who attributes it to the cooling action of the walls.

the propagation of the explosion-wave, making, of course, an assumption as to the specific heats of the gases formed at the temperature of the explosion. He pointed out how it might be possible to use the easily determined velocities of the explosion-wave to give the specific heats of the gases concerned. In 1906 Professor Jouguet, without knowing Mr. Chapman's work, developed on similar lines a very complete theory of the explosion-wave.* He has most justly chastised the want of mathematical rigour in my hypothesis and in that of Berthelot. We have reached the right result, he says, by a kind of chemical intuition. But as our results have led to M. Jouguet's generalisation, I, for one, will hope the verdict of my fellow-chemists will be: "Guilty, but please do it again." Fundamentally, I think, M. Jouguet and I have the same conception. We both think there is a preliminary heating up of the gas just before it burns; we both think that the wave-front is moving as a sound-wave with a velocity, relative to the unburnt gas in front, *twice* that calculated from the ordinary heat of combustion of the gases. But whereas I had supposed this increased velocity should be set down to increased temperature, M. Jouguet points out that the burning gas is driven forward *en masse* with the velocity of sound, and the wave-front is travelling like a sound-wave *in this moving gas*, and therefore has a motion relative to the unburnt gas in front double that of a sound-wave in the burning gases.

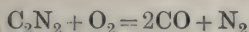
The theoretical conclusions of M. Jouguet concerning the forward motion of the gas behind the wave-front are entirely borne out by my photographic analysis of the explosion-wave. One can show the retardation of a sound-wave *meeting* the on-rushing burning gas; one can show that a sound-wave, following a little behind the wave-front, travels with almost the same velocity as the explosion-wave itself.

One other point of some importance: I found experimentally that an increase in the initial temperature of the unburnt gas was accompanied by a diminution in the rate of explosion. My formula did not account for this, but I find the equations of M. Jouguet lead to this result, when a moderate rise in the specific heats of the products of combustion is assumed.

Messrs. Chapman and Jouguet have raised the very important question whether the specific heats of gases at high temperatures can be calculated backwards from the observed velocities of explosion. I would point out that a determination of the velocity of the explosion-wave for one mixture would not definitely fix the specific heats of the products of combustion. For instance, if we

* *Journal de Mathématiques*, 1905-6.

take the simple case where cyanogen burns to carbon monoxide and nitrogen:



the velocity of the explosion-wave was found to be 2728 metres per second when the initial temperature was 10° . Working backwards from the observed velocity, I find that the mean specific heat of the products may lie between

$$4.5 + \frac{0.51}{1000}T \text{ and } 4.5 + \frac{0.6}{1000}T,$$

according as the compression of the gases is assumed to be more or less. The observed rate corresponds with the following pressures and temperatures:

Specific heat of CO and N_2 .	Pressure in atms.	Temperature, C.
$4.5 + \frac{0.51}{1000}T$	57.21	5966°
$4.5 + \frac{0.55}{1000}T$	51.21	5736°
$4.5 + \frac{0.60}{1000}T$	47.16	5541°

But by measuring the velocity of the explosion-wave when this mixture is "damped down" with inert nitrogen, or with argon, it is possible to limit the range of specific heats corresponding with the observed velocities, and also to compare the specific heats of nitrogen and argon at high temperatures. I am making experiments on these "retarded" explosions.

The exceptions to the application of Chapman's and of Jouguet's equations—for example, in the explosion of carbon monoxide and oxygen, where we believe on other grounds that steam intervenes; or in the complete burning of carbon compounds, where we have other reasons for believing that the formation of carbon dioxide is a secondary action—appear to me greatly to strengthen the view that the flame is propagated as a wave.

If, then, the flame in explosions of gases is really propagated as a pressure-wave, that is, by collisions of molecule with molecule, the chemical change involved in the wave-front must also proceed by these collisions; and since the wave does not wait for the rare occurrence of a triple collision, the primary chemical change must be uni- or bi-molecular, *not* termolecular. As Sir Joseph Larmor* has put the case, "Imagine the scale of magnitude of a gas at a pressure of one atmosphere to be magnified so that the diameter of each moving molecule becomes about one inch, there will be in the model roughly about one molecule in each cubic foot, and

* "On the Physical Aspects of the Atomic Theory." *Mem. Manchester Phil. Soc.*, 1908.

a molecule will have to travel about a hundred feet before it encounters another one. Such binary encounters will thus happen with some frequency, and from some of them combination may ensue. But the chance of three molecules coming together simultaneously is negligible; the only way in which a termolecular combination can arise is by one of the molecules attaching to itself another, and this pair going off together to meet a third. . . . It appears to be commonly recognised that direct termolecular combinations occur seldom; the inference from the present line of argument is that in gaseous reactions they do not occur at all."

It has been suggested that Sir J. J. Thomson's hypothesis—that chemical action in gases begins on the surface of condensed particles of liquid water—might be applied to the explosion-wave. I find it difficult to believe either that sufficient water particles can exist in the dried unburnt gas to allow the flame to proceed at the observed velocity, or, if such condensation really took place, that the velocity of explosion would not be *increased* by the addition of water vapour.

To sum up, I believe the reaction between hydrogen and oxygen in an explosion is a direct one, and does not take place through the intervention of steam, for three reasons, namely:

(i) That well-dried mixtures of electrolytic gas always explode with a spark;

(ii) That the velocity of explosion in a well-dried mixture is greater than when steam is added;

(iii) That the explosion-wave is propagated as a pressure-wave through the gas.

The Union of Hydrogen and Oxygen at Low Temperatures.

Whether steam or water facilitates the slow combustion of hydrogen and oxygen below the inflammation temperature is another question. The most careful experiments made to decide this question are those of Dr. Brereton Baker. In 1902 he described to this Society experiments in which he showed that when the greatest care had been taken to purify the gases, the moist gases exploded when the tube containing them was heated in a flame while the dried gases did not. In some of the tubes which did not explode, a small quantity of steam had been formed, and in one tube, which had been dried for two days only, water was visibly produced by slow combustion.

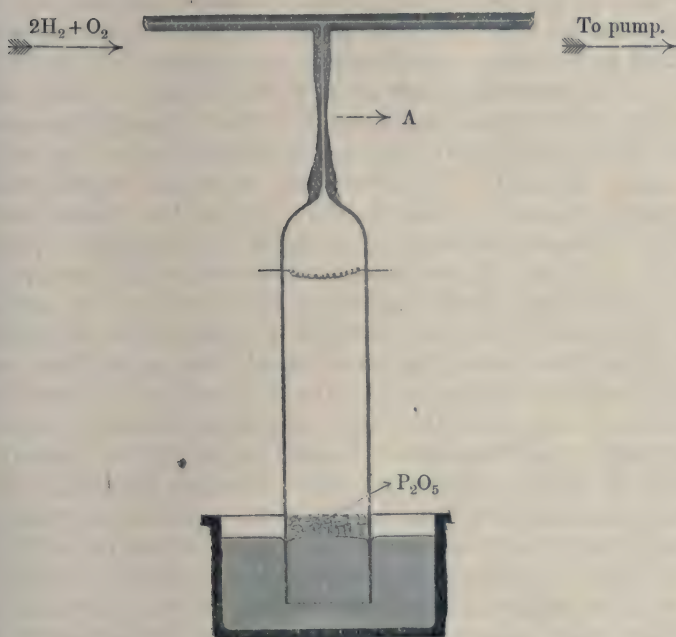
In another experiment Dr. Baker heated a fine silver coil in the dried gases, and succeeded in melting it without exploding the mixture.

The importance of these experiments induced me to repeat them,

and Dr. Baker was good enough to assist me by placing at my disposal an ingot of his pure silver, and some of his fifteen-times recrystallised barium hydroxide. To provide against the infirmities of age, I enlisted the services of Dr. E. C. Edgar (whose work on the atomic weight of chlorine proves his manipulative skill) to make an entirely independent series of experiments. As our experiments have not been published, perhaps I may be permitted to give a brief summary of them here.

The tubes, in which the gases were collected, were made of Jena glass; into the walls of these were fused platinum hooks, from

FIG. 1.



which hung coils of thin silver wire carefully drawn from Dr. Baker's ingot. The tubes were connected by a glass joint either directly to the electrolytic vessel, or to a condenser and drying tube sealed to that vessel. The tubes, as well as the other parts of the apparatus, were cleaned by hot chromic and nitric acids and by steaming; they were finally dried in a current of air.

The tubes were filled with electrolytic gas by placing them in a trough holding pure mercury (Fig. 1), and partly evacuating them until the mercury rose nearly to the silver; the gas was then slowly admitted. After several repetitions of this operation, the pieces

of phosphoric oxide (redistilled in oxygen) were introduced, and then the last traces of air were eliminated by again emptying and filling.

In other tubes no mercury was admitted, but after the admission of phosphoric oxide the glass was sealed off, and the air pumped out, while the tube and silver coil was maintained at a red heat. On cooling, the electrolytic gas was admitted, the pumping repeated, and the tubes, after being finally filled, sealed off. For the "dry" experiments, forty days were allowed before the silver coil was heated.

Dr. Edgar agrees with me in the following observations—(i) that a higher temperature was required to start the reaction in the dried than in the moist gas; (ii) that combination occurred both in the moist and in the dried gases, and that liquid water was deposited in the lower (cool) portion of the tube.

In four experiments performed by Dr. Edgar, he finally fused the silver wire without exploding the dried gases. His account, written at the time, says: "In each experiment, after the mercury had risen almost to the silver, the wire was fused without exploding the gases." I can entirely confirm this description. I watched the mercury rising in the tube and drops of water condensing; on raising the temperature of the wire, the mercury rose more quickly, and finally the silver fused without an explosion when the mercury was near the coil. I confess I did not think at the moment that, when the silver fused, the gas in the heated upper portion of the tube must have been mainly steam. On reflection it was clear that the experiment should be tried of attempting to melt the silver by *rapid* heating. Two of the tubes which had been drying for forty days exploded when the coil was suddenly heated to a bright red-heat. Our experiments show that, with the purity and dryness we were able to obtain (no doubt less perfect than in Baker's experiments), hydrogen and oxygen do not unite so readily as moist gases in contact with a heated silver wire, but such gases can be exploded by a sufficiently high temperature.

Professor Le Chatelier has defined the ignition point of gases as that temperature at which the initial flameless combination heats up the gas (more or less rapidly) until it inflames. Professor Nernst has given a similar definition. Below the ignition point, combination occurs, but the heat evolved is not sufficient to overcome the cooling effect of the surroundings. In a tube heated to 540° , for instance, electrolytic gas slowly combines, the amount of steam formed in unit time gradually diminishing as the change proceeds. At 560° the heat evolved by the more rapid combination

self-heats the mixture to the inflammation point. If the gas, however, can be maintained at 560° by contact with a sufficiently large surface, the combination proceeds as before, but more quickly. In those experiments, such as those of M. Hélier, in which electrolytic gas is drawn over small pieces of heated porcelain, exposing a very large surface to the gas, temperatures of 800° and higher can be employed without producing explosion.

In the experiments which Dr. Coward and I published last year on the ignition point of gases, we brought together hydrogen, heated in an inner tube, and oxygen, heated in an outer tube: we found it necessary to use a wide outer tube for the oxygen, and a certain rapidity of flow of the hydrogen in the inner tube in order to obtain a constant ignition point. When the region where the heated gases mingled was removed from contact with a heated surface, a minimum ignition temperature was obtained. When the gases met close to a heated surface, the ignition point was raised. That electrolytic gas can combine isothermally at high temperatures if the surface contact is large is a sufficient explanation of these observations.

Now the question raised by Dr. Baker is this: Is the initiation of slow combustion in electrolytic gas, and the velocity of the reaction when it is started, influenced by the presence of steam or water particles? In his latest experiments he has found that when moist hydrogen and nitrous oxide are kept at 530° , the presence of an ionising agent, such as thoria or radium bromide, greatly increases the rapidity of the reaction; in the carefully dried gases the ionising agent had no effect.

Although I agree with Dr. Baker that steam (or water) intervenes in the initial action of hydrogen on oxygen at moderate temperatures, I do not think it necessary for the propagation of a flame once started in the mixture. There are many similar differences in gaseous reactions. Light will not explode dried hydrogen and chlorine, it does so in presence of water; but once start a flame in mixed hydrogen and chlorine, and it is propagated as an explosion-wave through the dried gases. A platinum wire heated to whiteness will not fire a mixture of cyanogen and oxygen, flameless combination taking place round the wire; but a spark immediately sets up the explosion-wave in the same mixture.

What is the First Product of the Union of Hydrogen and Oxygen in Flame?

Do hydrogen and oxygen directly form steam, or do they form hydrogen peroxide in a flame? If we accept the view of Mendeléeff that all primary reactions between different substances

are bimolecular—a view enforced by Sir J. Larmor for gaseous reactions—we must suppose that a collision between a hydrogen and an oxygen molecule can only result in the primary formation of hydrogen peroxide, or in the formation of steam and a free oxygen atom.

The following reasons, among others, have been brought forward for the view that hydrogen peroxide is the first product in flame:

(i) That hydrogen peroxide is found in the water rapidly condensed from a hydrogen flame;

(ii) That the mixture of equal volumes is more sensitive to a spark;

(iii) That the mixture in equal volumes has a lower ignition point than any other mixture.

(I.) As, I think, Moritz Traube first showed, a jet of burning hydrogen playing on to the surface of water produces peroxide in the water. Some years ago, when I repeated Traube's experiment, I thought that the mere heating of the water would produce some peroxide, but I found afterwards that this was incorrect. It requires some burning to take place near the surface of the water. But the presence of the peroxide in the condensed water might be explained either by its direct formation from hydrogen and oxygen, or by the union of the liberated oxygen atom with a molecule of water. Those who favour the first view consider the peroxide to be dihydroxyl, $\text{H}-\text{O}-\text{O}-\text{H}$, those who take the second view consider

the peroxide to be oxygenated water,

$$\begin{array}{c} \text{H} \\ | \\ \text{O}=\text{O} \\ | \\ \text{H} \end{array}$$

There are reactions of hydrogen peroxide (and of alkaline peroxides) which may be appealed to in support of both views: possibly both forms may exist in solution. The second formula seems to me to be supported by the remarkable researches of Carl Harries on the decomposition of ozonides by water, in which he shows that the loosely joined oxygen atoms attach themselves to water molecules to produce hydrogen peroxide quantitatively.

The recent experiments of Manchot* confirm the older observations that ozone as well as hydrogen peroxide exists in a hydrogen flame. If the ozone is formed owing to the liberation of an oxygen atom, hydrogen peroxide may be formed by the union of an oxygen atom with steam. Engler's experiment of burning a hydrogen jet so as to bore a hole into ice, shows plenty of peroxide in the condensed water in the hole. I have repeated this experiment both with ice and with a lump of solid carbon dioxide. When a large jet of hydrogen is used,

* *Ber.*, 1909, 42, 3948.

burnt with an outside blast of air, and a very small jet of nitrous oxide is introduced into the centre of the hydrogen flame, a piece of ice may be introduced so that it is surrounded by hydrogen, and a hole may be bored in it by the small central jet of nitrous oxide burning in hydrogen. The central jet may then be fed by oxygen, and the samples of condensed water compared. While the oxygen produces plenty of peroxide, only a trace is found in the water condensed from the nitrous oxide flame. This, of course, only shows that in the burning of hydrogen and nitrous oxide, steam is formed directly without the splitting off of an oxygen atom.

In the explosion-wave the greatest velocity of propagation is not given by electrolytic gas. The addition of hydrogen increases the velocity of the wave so long as it is set up in the mixture; this, of course, is due to the mobility of the hydrogen. But the fact that the addition of equal volumes of oxygen and nitrogen to electrolytic gas retards the wave exactly in proportion to their density is an argument that hydrogen peroxide is not the primary product of the change, for the two gases appear to be equally inert to the mixture $2\text{H}_2 + \text{O}_2$.

Consider the explosion-wave traversing the mixture $\text{H}_2 + \text{O}_2$. If hydrogen peroxide were directly formed, the immensely high temperature of the flame and the very rapid cooling behind the flame should be precisely the conditions most favourable for a high yield of the endothermic peroxide. I have carefully examined the products of combustion of the explosion-wave in such mixture, and could detect no peroxide. On the other hand, when the explosion-wave traverses electrolytic gas, about 1 per cent. of unburnt gas is left behind, showing how rapid the cooling is.

II. The experiments of Emich on the sensibility to explosion by small sparks of different mixtures of hydrogen and oxygen led him in 1897 to suggest that hydrogen peroxide was the first product of the reaction on the ground that the mixture in equal volumes was most sensitive to the spark. In a later paper (1900) he withdrew this conclusion, although his work is still quoted as an argument in favour of the direct formation of peroxide. Whether or not a local heating of a small mass of gas by a spark will set up general inflammation must depend *inter alia* on the rate at which heat is conveyed away from the heated region; a gas richer in the rapidly moving hydrogen molecules will convey heat away more quickly than one poorer in hydrogen. Dr. Coward has recently found that the mixture in equal volumes is not the most sensitive to a spark. The addition of oxygen still further increases the sensibility.

III. But a stronger argument has been drawn by K. G. Falk* from his experiments on the ignition point of gaseous mixtures heated by adiabatic compression. Acting on the very ingenious suggestion of Professor Nernst, he has compressed different mixtures of hydrogen and oxygen in a steel cylinder by means of a weight falling on a piston, and has determined the volume of the compressed gas by measuring the lowest point reached by the piston. He considers the whole mass of gas is heated equally throughout until it reaches the ignition point, and then that the whole detonates practically instantaneously, when the explosion stops the descent of the piston. On the assumption that the piston had no time to move downwards appreciably after the ignition point was reached, he calculates the temperatures of ignition of different mixtures:

Mixture.	Ignition point.
$4\text{H}_2 + \text{O}_2$	605°
$2\text{H}_2 + \text{O}_2$	540
$\text{H}_2 + \text{O}_2$	514
$\text{H}_2 + 2\text{O}_2$	530
$\text{H}_2 + 4\text{O}_2$	571

The last four figures are plotted out, and the dotted curve drawn through them on page 676. Falk says: "The fact that the maximum affinity is shown by the mixture $\text{H}_2 + \text{O}_2$, proves that H_2O_2 must be the first product of the reaction between hydrogen and oxygen."

Falk gives as his reasons for the assumption that the gas detonates instantaneously throughout its whole mass, once the ignition temperature is reached, the fact that the explosions are of great violence, and that the compression was very nearly the same in the case of electrolytic gas whether the weight fell from a lower or a higher altitude. What he found to be nearly true of the rapidly-firing mixtures, $2\text{H}_2 + \text{O}_2$ and $\text{H}_2 + \text{O}_2$, he has assumed to be also true of the less rapidly-firing mixtures with excess of oxygen, and of mixtures of hydrogen and air.

When I read Falk's first paper, it occurred to me that the descending piston must send in front of it sound-waves, which would be reflected from the bottom of the cylinder back to the piston again, and so on, producing by their collisions zones of higher temperature, at one of which the flame would eventually start. Falk states in his second paper that Professor Jouguet has made the same criticism. By photographing the explosion produced by the adiabatic compression on a rapidly-moving film, I have shown that the flame *does* start from a point, and in the more slowly burning mixtures the spread of the flame throughout the gas takes an appreciable time. Moreover, the point of ignition can be made to

* K. G. Falk, *J. Amer. Chem. Soc.*, 1906, 28, 1517; 1907, 29, 1536.

vary by altering the velocity of the piston. With electrolytic gas the photographs show that the explosion-wave is very quickly set up, but the flame always starts *from one point*. The mass of the gas is *not fired instantaneously*, although the time required in this case for the flame to reach the piston is negligible. With such a mixture as $H_2 + 2O_2$, the time required to set up the explosion-wave is *not* negligible.

If we accept Nernst's definition of the ignition point of a mixture of gases as that temperature at which a mass of the gas *rapidly* self-heats itself by combination until it bursts into flame, and if this flame starts *at some point* in the mixture and spreads from that point, there will be two periods during which the piston may continue to move after the "ignition point" has been reached: (i) the period from the beginning of rapid self-heating until the flame appears; and (ii) the period required for the flame to spread through the gas and stop the descent of the moving piston.

Just as the time required for the flame to set up the explosion-wave differs in different mixtures, so does the time required for the self-heating from Nernst's "ignition point" to the actual appearance of the flame.

When a mixture of air and hydrogen (5 vols. to 2) was compressed in the cylinder, and the descent of the piston was arrested by means of a steel collar, I found the ignition temperature a few degrees only above that of electrolytic gas. This was in agreement with our previous determinations at atmospheric pressure. But when the piston was allowed to descend until it was stopped by the explosion of gases, as in Falk's experiments, I could obtain ignition points, not only as high as Falk's (649°), but, by increasing the velocity of the piston, I got temperatures of 700° , 800° , or 900° at pleasure. A similar variation was found for the mixture $H_2 + 4O_2$.

It was evident that the error due to the movement of the piston during the "pre-flame" period of self-heating might be far greater than the error due to the movement of the piston *after* the flame had started.

In determining the temperatures of ignition of mixtures of hydrogen and oxygen, it was necessary, therefore, to stop the descent of the piston artificially the moment the gases were brought to the self-heating temperature. This was effected by having on the end of the piston a steel head, which was caught by a steel collar at a certain point in its descent. By varying the thickness of the collar, the piston could be stopped at any point. By a series of trials a compression was found which fired the mixture, and a slightly less compression, which did not. The mean between the two was taken

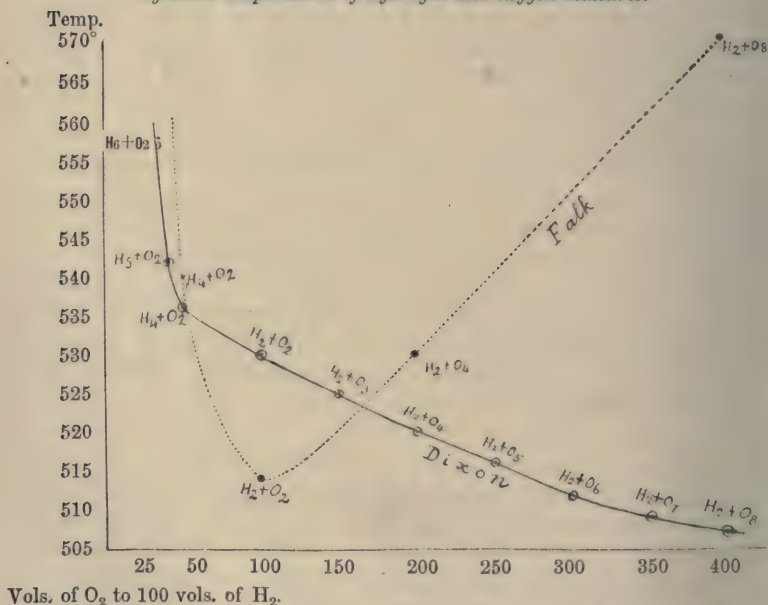
as the ignition point. On repeating each experiment several times, nearly concordant ignition points were obtained.

For the sake of comparison with Falk's numbers, I have calculated the mean ignition points from my compression-volumes, using the same ratio of the specific heats ($\gamma=1.40$) as Falk has done. The temperatures so calculated are plotted in Fig. 2 with the continuous curve drawn through them:

Mixture.	Ignition points ($\gamma=1.40$).	Mixture.	Ignition points ($\gamma=1.40$).
H_6+O_2	557°	H_2+O_4	520°
H_5+O_2	542	H_2+O_5	516
H_4+O_2	536	H_2+O_6	512
H_2+O_2	530	H_2+O_7	509
H_2+O_3	525	H_2+O_8	507

FIG. 2.

Ignition temperatures of hydrogen and oxygen mixtures.



My ignition point for electrolytic gas agrees closely with that found by Falk, an agreement which shows that this mixture must have a very short period of flameless combustion, and the spread of the flame must be very rapid. I find the mixture in equal volumes has a lower ignition point than electrolytic gas, but it is not the mixture of "maximum affinity." The further addition of oxygen regularly lowers the ignition point. I would submit, therefore, that

the ignition points of hydrogen and oxygen mixtures do not prove that hydrogen peroxide is the first product of the reaction.

I began this address with a note of warning, and would wish to end on the same note. I have spoken of the use of hypotheses and hinted at their abuse. In criticism it has been my desire—at least since the fierce invectives of youth lost their sweetness—to be gentle with my adversary's and stern with my friend's hypothesis.

If ever any of my old research students look back on my criticisms of their work with feelings from which time has removed the bitterness, I think they will admit that at least I saved them from the publication of hypotheses, useful perhaps at the time, but certainly untenable in the light of fuller knowledge.

OBITUARY NOTICES.

CHARLES GRAHAM.

BORN SEPTEMBER 4TH, 1836; DIED NOVEMBER 13TH, 1909.

THIRTY years ago, few names were more prominently identified with the science and technology of brewing and malting in this country than that of the subject of this memoir, and there are not many men to whom those industries owe a heavier debt of gratitude. Many greater investigators in this department of applied science there have been: men whose researches have earned for them almost world-wide renown, but it is to the everlasting credit of Graham that he was one of the earliest to recognise how greatly science could aid in the development of the great industries to which he devoted the best part of his life, and that he succeeded in bringing home that all-important fact to large numbers of men who were steeped in empiricism, and suffering from the paralysing influence of an unjustified complacency. From an early age, Graham manifested an intense love of natural science, and having as a very young man decided to adopt chemistry as a profession, he entered the Chemical and Agricultural College at Kennington, where he worked under Mr. Nesbit, devoting his attention to analytical chemistry in general, and to agricultural chemistry in particular. With a view to graduating at the University of London, he a few years later entered University College as a student, and in 1864 took the degree of Bachelor of Science. About this time he was appointed an assistant to Dr. A. W.

Williamson, then Professor of Chemistry at that College, and in 1866 he received the degree of Doctor of Science at the University of London. Early in 1867, while still engaged at University College, he was invited by Baron H. von Rath, a Member of the Reichsrath and President of the Rhenish Agricultural Society, to act as resident chemical adviser at his mining works in Nassau. Graham accepted that position, and was a little later appointed arbitrator in chemical matters between the German mine owners and the English contractors. During this period Graham's attention was largely devoted to a study of the Nassau phosphate deposits, and to questions connected with the chemistry of soil and to the rationale of artificial manuring. During the years 1868-1870 he published, in German agricultural journals, a number of papers on those subjects, all of which recorded painstaking and sound work, and several of which afforded evidence of that scientific "prevision" which was so noticeable a characteristic in later years. These papers attracted a good deal of attention at the time, and on the expiration, in 1870, of his German engagement, he was invited to proceed to Spain to examine and report on some extensive mining properties in that country. On his return to England a few months later, Graham resumed his tutorial work at University College, and at the same time supplemented his income by carrying on an analytical and consulting practice, and it was then that he seriously turned his attention to the science of brewing and to the technology of the fermentation industries generally. On December 8th, 1873, he delivered the first of his well-known Cantor lectures, "On the Chemistry of Brewing," and the remaining four of the series were given on December 15th, and in the following February. These were delivered before large audiences at the Society of Arts, were widely reproduced in the trade and other journals, and produced a great impression. It was not that they contained much that was strikingly novel, and certainly nothing that was epoch-making, but they were well modelled, and admirably calculated to effect their main object, namely, to make the practical man *think* for himself. At the end of the concluding lecture, Graham said: "After all, it (that is, this course) has only been suggestive. Its main object has been to raise discussion, and excite inquiry. . . . My criticisms, however, have been solely actuated by a desire to make you look at the matter from a new standpoint, so that you might see the rationale of the processes employed." In a very direct and personal sense, these lectures certainly did "excite inquiry," and, as a result, Graham speedily built up a large consulting practice among brewers, maltsters, vinegar makers, and

others; but they had a far more widely reaching effect, for they tended in no small degree to accelerate the decline of empiricism and quackery, and to stimulate the spirit of inquiry and research. That they contained many views which are not altogether in accord with our modern knowledge is not to be wondered at, but they were models of clear subject arrangement, were characterised by lucidity of treatment, and were occasionally illuminated by flashes of what, for want of a better term, must be called scientific foresight or prevision. In fact, not a few processes which are of comparatively recent introduction into brewing and malting practice will be found to have been suggested, or at least adumbrated, in those lectures. Six years later, that is, in 1879, Graham attempted to do for bakers what he had already done for brewers and maltsters, and delivered before the Society of Arts a second series of Cantor lectures, "On the Chemistry of Bread Making." These were modelled somewhat on the lines of his brewing lectures, and, in the words of the presiding chairman, were "not unworthy to take a place by the side of his former course." Graham was always keenly interested in the work of the Society of Chemical Industry, and at the first general meeting of that Society in June, 1881, communicated a paper on Lager Beer, which was a serious attempt to make the English public acquainted with the virtues and properties of the low-fermentation beers as made and consumed on the Continent. For a comparatively short communication, this paper contains a vast amount of information, and can even now be studied with advantage.

In 1878 Graham was appointed Professor of Chemical Technology at University College, London, and in that capacity had to deal with the application of chemistry to a number of industries. Courses of study were laid down for metallurgists, alkali, soap and manure manufacturers, manufacturers of glass, cement, artificial stone, etc., bleachers, dyers and calico printers, brewers, distillers, and vinegar manufacturers, agriculturalists, and consulting chemists and public analysts. Special courses of lectures were given on the chemistry of the alkali trade, on the chemistry of brewing, and on agricultural chemistry, of which by far the most important and most numerous attended were those devoted to the chemistry of brewing and malting. That Graham's life at this time was a busy one may easily be imagined, for in addition to his exacting professorial duties at University College, including, of course, both lectures and laboratory instruction, he carried on a large consulting practice, and was, moreover, for more than thirteen years County Analyst under the Sale of Food and Drugs Acts for the three divisions of Lincolnshire. In 1889 Graham

resigned his Chair with the title of Emeritus Professor, and carried on, in association with the writer of this memoir, a private consulting practice, chiefly in relation to the fermentation industries. At the end of about ten years he retired to Hastings, where he lived very quietly, and where he died on November 13th last, at the age of seventy-four.

He was an old Member of the Chemical Society, having been elected in 1862, and served on the Council during the years 1880-1881. He was also an original Fellow of the Institute of Chemistry, and had been a Vice-President and an Examiner of that body. Graham was a man of iron will and of immense force of character, and, like many such men, was apt to conceive violent likes and dislikes, which, so far as an outside observer could judge, were frequently without justification. In scientific matters cautious to a fault, and never sparing any pains himself in endeavouring to arrive at the truth, he was angrily impatient of all who, through defective powers of observation, intellectual laziness, or carelessness, communicated to him statements which he knew to be incorrect. He was a man of wide scientific attainments, and possessed a large fund of hard common sense, qualities which rendered his advice (not always confined to purely technical matters) of the greatest value to his numerous clients. Easily moved to anger by opposition, direct in his speech, and often brusque in his manner, he was, nevertheless, capable of forming real attachments, and was the author of many acts of unostentatious kindness. Throughout his life, however, his main affection centred in his old College, and those who knew him at all well will hardly have been surprised that at his death he should have bequeathed to it the bulk of his estate. Apparently strong and vigorous, he yet knew much of physical suffering, and one cannot help feeling that there is some connexion between that fact and the terms of his bequest, namely, that it should be devoted to the encouragement of research, having for its object "the prevention, cure, or alleviation of human disease and suffering."

A. CHASTON CHAPMAN.

THEOPHILUS HORNE REDWOOD.

BORN JULY 31ST, 1849; DIED MARCH 31ST, 1909.

THEOPHILUS HORNE REDWOOD, the second son of Dr. Theophilus Redwood, was born on July 31st, 1849. He was educated at University College School, and received his instruction in chemistry in the laboratory of his father, who was Professor of Chemistry at

the Pharmaceutical Society. For many years he acted as assistant to his father, and then turned his attention to industrial chemistry, accepting an appointment as chemist on the lime plantations of Messrs. Sturge on the island of Montserrat, West Indies. Subsequently he became associated with the important undertaking now known as Borax Consolidated.

He possessed unusual artistic taste, which he turned to good account in cultivating the art of landscape photography long before the days of films and dry plates. He was elected a Fellow of the Royal Photographic Society in 1896.

He suffered from a congenital malformation of the spine, which in his later years caused partial loss of power in the lower extremities, and otherwise prejudicially affected his health, but his affliction was borne uncomplainingly, his hopefulness, cheerfulness, and sense of humour being maintained to the last.

Although of remarkable keenness of intellect, he was an exceptionally modest and unselfish man, always taking a kindly and active interest in the welfare of others, and at all times ready with encouragement and sympathy. He had, indeed, a charming disposition, was loved by all who knew him intimately, and never made an enemy.

Although for the last two or three years of his life he was practically confined to his house, he was contemplating another visit to the islands of the West Indies, when he had an attack of pneumonia, to which he succumbed on March 31st, 1909.

He leaves a widow, two sons and two daughters.

B. D.

SIR THOMAS WARDLE.*

BORN JANUARY 26TH, 1831; DIED JANUARY 3RD, 1909.

SIR THOMAS WARDLE was born at Macclesfield on January 26th, 1831. He was the eldest son of Mr. Joshua Wardle, of Cheddleton Heath, near Leek, who founded the silk dye works of Joshua Wardle and Son, at Leek Brook, when Sir Thomas was scarcely a year old. Educated at Macclesfield and Leek, he entered his father's business, and his early energies soon bore fruit in the well-being of the firm. His efforts in life were not destined to be restricted to one particular channel, for soon after the death of his father he brought into being the silk and cotton printing business of Wardle and Co., at Hencroft, Leek. Sir Thomas Wardle was a keen student of chemistry, geology, and archæology, and later on of sericulture, and his tastes ranged over an even wider field.

* Abridged, by permission, from the *Journal of Indian Art and Industry*

The first dealing Sir Thomas had with Indian products was the trial he made, at the instigation of Sir George Birdwood, to utilise Tasar silk, the wild silk of India, and to make it a marketable commodity. As a result of his experiments he succeeded in bleaching the brown fibre and in dyeing it with such perfection as to make it serviceable in the manufacture of fabrics. For several years a Wardle collection of bleached and dyed Tasar silks was on exhibition at Lyons, and this was shown in the British section of the 1878 Paris Exhibition. Sir Thomas became a juror at this International Exhibition, and had the honour to be appointed a Chevalier of the Legion of Honour.

At the instigation of Sir George Birdwood, the Secretary of State in the year 1885 sent Sir Thomas Wardle out to India in order to make a typical collection of silk textiles and native embroideries for the Silk Culture Court of the Colonial and Indian Exhibition, and he was also requested to visit the Bengal silk districts and to make a report on sericulture. As an outcome of the inquiry, it was brought to light that 60 per cent. of the silkworms died of preventible diseases, and that the reeling from the cocoons in the filatures was very imperfect.

In the year 1887 he accepted the position of Chairman to the Silk Section of the Manchester Jubilee Exhibition, and, chiefly through his energies, a display of silk manufacturing processes from the reeling of cocoons onwards was exhibited. It was from this exhibition that the Silk Association of Great Britain and Ireland came into existence, with Sir Thomas Wardle as its president, and to this honourable post he was elected, without intermission, year after year, until his death in 1909.

During the year 1896 Lieut.-Colonel Sir Adelbert Talbot, K.C.I.E., was appointed Resident in Kashmir, and, as a result of his study of Sir Thomas's encouraging reports on the possibilities of Kashmir silks, he recommended H.H. the Maharajah of Kashmir to commence the industry on a commercial basis and in a scientific and extensive manner. In 1897 Sir Thomas was requested to consult with Sir George Birdwood at the India Office on the subject, and subsequently he was sent to France and Italy to select the best races of silkworm eggs, and to acquire the very best reeling machinery, as well as to find a suitable person to direct operations in Kashmir.

In the year 1897, at the instance of Lord Salisbury, he received from her Majesty the Queen the honour of knighthood for the work he had given to India and the silk industry generally.

From the year 1897 the sericulture in Kashmir progressed and went ahead by leaps and bounds, and in 1900 the output of raw silk

was 57,921 lbs.; in 1901 it increased to 90,648 lbs.; and in 1902 it reached the very creditable figure of 135,221 lbs.

At a later date Sir Thomas Wardle strongly advocated the commencement of silk weaving in the State, and he was instructed, with the Maharajah's sanction, to send out from England the plant necessary for an initial factory, and the first instalment was 200 looms, together with a young and capable weaver from Macclesfield to superintend the preliminary stages. Success proved to be in the wake of this venture, and at the present time scientific weaving takes place daily at Srinagar.

One of the most important honours, and certainly the one that gave Sir Thomas Wardle one of his greatest pleasures in life, was his admission by the Worshipful Company of Weavers to the honorary freedom of the Weavers' Company on February 3rd, 1903. He was then able to acquire the Freedom of the City of London.

Sir Thomas Wardle wrote many monographs on scientific and technical subjects. He added a learned chapter in the geology of Leek and district to the first edition of the "History of Leek," by John Sleigh, published in the year 1862. His splendid collection of carboniferous limestone fossils he gave to the Nicholson Institute at Leek. Other works on geology were: "Geology of the Roches," "Geology of Shuttlingslowe," "Geology of Mid-England." He also wrote on the technical aspects of artistic weaving, and his monograph on "The Present Development of Silk Power-loom Weaving in France" was the outcome of a visit to Lyons in 1893 to investigate the subject. His works on silk and the silk industry were most numerous, the most important being "Report on the English Silk Industry," "Silk: its Entomology, History, and Manufacture," "History and Growing Utilisations of Tasar Silk," "The Wild Silks of India," "The Dyes and Tans of India," "The Adulteration of Silk by Chemical Weighting," "Kashmir: its New Silk Industry," etc., and his last work was a monograph on the "Divisibility of Silk Fibre," published in 1908.

Sir Thomas Wardle died peacefully at his Leek residence on January 3rd last year, in his seventy-eighth year, surviving his wife by seven years. He always lived a life of high pressure, he worked well, and played well, and it was doubtless in consequence of this judicious combination of the two that he was enabled to live a life of almost youthful activity. It was only six months from his death that the strain perceptibly told on him, and from that period he gradually sank and passed away.

ALEXANDER FORBES WATSON.

BORN JANUARY 16TH, 1872; DIED AUGUST 4TH, 1909.

ALEXANDER FORBES WATSON, Chief Chemist in the Brewery of Messrs. Arthur Guinness, Son and Co., Ltd., died on August 4th, 1909, in his thirty-eighth year, as the result of an accident at Ferbane, King's Co., Ireland.

He was born in Edinburgh on January 16th, 1872, and received his early education at George Watson's College in that city. In 1889 he began to study chemistry at Surgeon's Hall, Edinburgh, and the Heriot-Watt College, where Prof. W. H. Perkin, jun., occupied the chair of chemistry. He then entered the University to become a student under Prof. Crum Brown, and graduated B.Sc. in 1893, in which year he was also appointed a University Assistant. During his career as a student he gained the Hope Scholarship, and in 1894 the George Heriot Fellowship.

In pursuit of an intention to devote himself to some branch of technical chemistry, Mr. Watson turned his attention to biochemical problems in connexion with brewing, and in order to acquire a special knowledge of mycological work, he spent some time in the laboratory of Alfred Jörgensen in Copenhagen, and also in that of Dr. Mach, of the Scientific Institute of San Michèle, where a study of wine yeasts could be made. On his return to Edinburgh, Mr. Watson was appointed Lecturer on Fermentation in the University, but his tenure of this post ceased in 1896, when he took up his appointment as Chemist to Messrs. Guinness.

Although Mr. Watson as a chemist was probably not widely known, those who had any acquaintance with the extent and variety of his professional work knew him for a man of distinction in all that he did. The problems of a great brewery call for an application of almost every branch of chemistry, and Mr. Watson, encouraged by a sympathetic directorate, was not slow to demonstrate the interpretative powers of laboratory experiments in their bearing on practice. His success was largely due to his faculty of adhering to strictly scientific methods, while never failing to steer his investigations according to the practical object in view. In the biochemical industries this is, perhaps, a much more difficult proposition than it is generally known to be; at any rate, the chemist who would be a success in an essentially conservative industry like brewing must be ever ready to justify his science by what it can add to practical experience, instead of producing results which may be only interesting and suggestive. From such a point of view, Mr. Watson was one of the most able technical

chemists of his day, and although his work as an investigator was compressed into a few short years, its soundness and thoroughness have probably not been surpassed, even in an industry which is justly celebrated for the high standard of its scientific work.

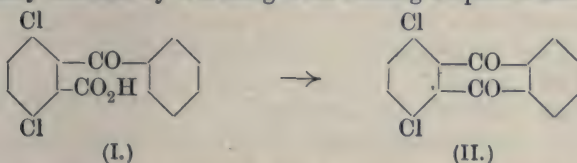
J. H. M.

XLV.—1 : 4-Dichloroanthraquinone and Its Derivatives.

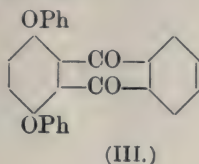
By GERTRUDE MAUD WALSH and CHARLES WEIZMANN.

NAPHTHACENEQUINONES prepared by the condensation of 3 : 6-dichlorophthalic anhydride and α -naphthol, and the elimination of water from naphthoylbenzoic acid, have been previously described (Harrop, Norris, and Weizmann, *Trans.*, 1909, **95**, 279), and also the anthraquinones from 3 : 6-dichlorophthalic anhydride and the three xylenes (Harrop, Norris, and Weizmann, *ibid.*, 1312). The present communication deals with the parent quinone and 1 : 4-dichlorohydroxymethylantraquinones derived from *o*-, *m*-, and *p*-cresols. The condensation of 3 : 6-dichlorophthalic anhydride and benzene was carried out by Le Royer (*Annalen*, 1887, **238**, 356), but he did not prepare the corresponding quinone. 1 : 4-Dichloroanthraquinone has been isolated by Hammerschlag (*Ber.*, 1886, **19**, 1109), and was also obtained by Graebe (*Ber.*, 1900, **33**, 2019). In order further to characterise this quinone, several of its derivatives have been prepared.

The condensation of dichlorobenzoylbenzoic acid (I) to the quinone (II) is easily effected by warming with fuming sulphuric acid.

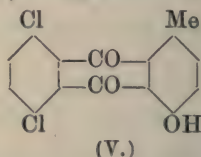
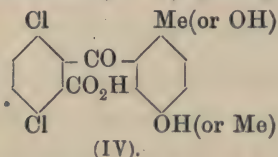


When warmed with concentrated nitric acid in presence of a little fuming sulphuric acid, 1 : 4-dichloroanthraquinone yields a *mononitro*-derivative, which is easily reduced to the corresponding amino-compound by tin and acetic acid. When heated with fuming sulphuric acid, 1 : 4-dichloroanthraquinone forms a *monosulphonic acid*. The two chlorine atoms are readily displaced by phenoxy-groups when heated with excess of sodium phenoxide, furnishing the corresponding 1 : 4-*diphenoxyanthraquinone* (III) :



The condensation of 3:6-dichlorophthalic anhydride with *o*-, *m*-, and *p*-tolyl methyl ethers by means of aluminium chloride, and the subsequent closing of the ring by fuming sulphuric acid to produce the desired quinones, does not proceed so smoothly and satisfactorily as in the case of the formation of 1:4-dichloroanthraquinone.

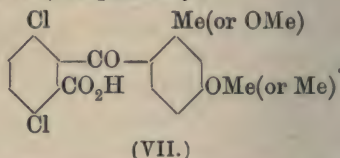
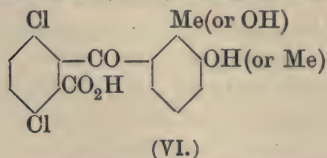
3:6-Dichloro-5'(or 6')-hydroxy-2-o(or *m*-)-toluoylbenzoic acid (IV)



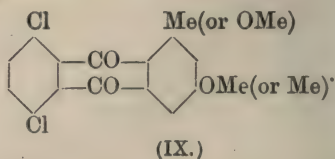
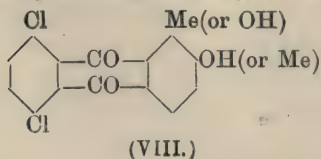
is prepared from 3:6-dichlorophthalic anhydride and *p*-tolyl methyl ether in presence of aluminium chloride. Most of the acid is hydrolysed during the reaction, and part of it is converted into the corresponding quinone. When treated with a molecular proportion of bromine in warm acetic acid solution, this acid forms a *monobromo*-derivative, which, on dissolving in warm fuming sulphuric acid, gives probably the corresponding bromo-quinone, but the yield is poor, and it was not found possible to obtain this quinone in sufficient quantities for analysis. By the removal of water from the above 3:6-dichloro-hydroxy-2-toluoylbenzoic acid, 1:4-dichloro 8-hydroxy-5-methylantraquinone (V) is obtained in small yield.

The replacement of the two chlorine atoms by phenoxy-groups does not take place so easily as in the case of the parent quinone (II). The presence of copper powder is necessary, and even then only one of the chlorine atoms is attacked. With phenyl mercaptan, even in the presence of copper powder, no substitution occurs.

3:6-Dichlorophthalic anhydride condenses with *o*-tolyl methyl ether and also with *m*-tolyl methyl ether to form 3:6-dichloro-3'(or 2')-hydroxy-2-o(or *m*-)-toluoylbenzoic acid (VI) and 3:6-dichloro-4'(or 2')-methoxy-2-o(or *p*-)-toluoylbenzoic acid (VII) respectively:

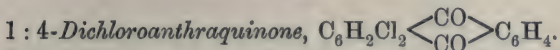


These two acids when treated under the conditions described in the experimental part of this paper lose water and form the corresponding methylantraquinones (VIII and IX):



The latter (IX) is, however, produced in such very minute quantities that sufficient has not yet been obtained for analysis.

EXPERIMENTAL.



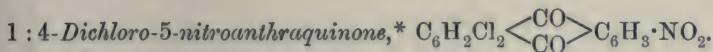
The quinone is obtained by heating 50 grams of 3 : 6-dichlorobenzoylbenzoic acid with 50 grams of boric acid, together with an excess of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide), to 100° for a few minutes. After cooling, the mass is poured on ice and filtered. Traces of unchanged acid are removed by boiling dilute sodium hydroxide, and the quinone is finally purified by crystallisation from glacial acetic acid, from which it separates in yellow needles, melting at 186° :

0.1493 gave 0.3291 CO_2 and 0.0293 H_2O . $C = 60.12$; $H = 2.18$.

0.1512 „ 0.1539 $AgCl$. $Cl = 25.18$.

$C_{14}H_6O_2Cl_2$ requires $C = 60.64$; $H = 2.16$; $Cl = 25.63$ per cent.

1 : 4-Dichloroanthraquinone is soluble in benzene, alcohol, or acetic acid.



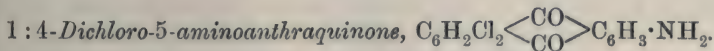
1 : 4-Dichloroanthraquinone is dissolved in concentrated nitric acid containing a little fuming sulphuric acid, and gently warmed for five minutes. The deep yellow solution is poured into water, when the nitro-compound crystallises out. On recrystallisation from glacial acetic acid it melts at 238°. It is readily soluble in benzene, but insoluble in methyl alcohol. From acetic acid it separates in minute, yellow needles :

0.1343 gave 0.2559 CO_2 and 0.0165 H_2O . $C = 51.98$; $H = 1.37$.

0.1587 „ 6.7 c.c. N_2 (moist) at 18° and 740 mm. $N = 4.70$.

0.1221 „ 0.1068 $AgCl$. $Cl = 21.65$.

$C_{14}H_5O_4NCl_2$ requires $C = 52.17$; $H = 1.55$; $N = 4.35$; $Cl = 22.05$ per cent.



This is prepared by reducing the nitro-quinone just described with tin in acid solution. The nitro-compound is dissolved in acetic acid, tin added, and the mixture heated, when the liquid assumes a crimson colour. The product is poured into water and neutralised

* From analogy to anthraquinone the nitro-group probably occupies the 5-position.

with sodium hydroxide, when the base separates in red needles, melting at 199° :

0.1440 gave 6 c.c. N_2 (moist) at 17° and 748 mm. $N = 4.75$.

$C_{14}H_7O_2NCl_2$ requires $N = 4.79$ per cent.

The *acetyl* derivative is obtained by heating the base with excess of acetic anhydride in presence of pulverised zinc chloride. The product is poured into water, and the resulting precipitate is collected and purified by crystallisation from xylene, from which it separates in yellow needles, melting at 178° . With concentrated sulphuric acid it gives a red coloration :

0.1584 gave 6.4 c.c. N_2 (moist) at 15° and 746 mm. $N = 4.61$.

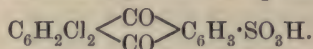
$C_{16}H_9O_3NCl_2$ requires $N = 4.18$ per cent.

The *acetate* of 1 : 4-dichloro-5-aminoanthraquinone melts at 185° :

0.1834 gave 0.3678 CO_2 and 0.0580 H_2O . $C = 54.69$; $H = 3.53$.

$C_{16}H_{11}O_4NCl_2$ requires $C = 54.54$; $H = 3.12$ per cent.

1 : 4-Dichloroanthraquinone-6-sulphonic Acid,



This acid was isolated in the form of its sodium salt in the following manner: One part of 1 : 4-dichloroanthraquinone was mixed with two parts of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide), and heated in an oil-bath ($150-180^{\circ}$) until a drop of the mixture gave a clear solution in water. The product was then cooled and poured into water, neutralised with sodium carbonate, and evaporated, when yellowish-brown crystals of the sodium salt appeared :

0.1528 gave 0.0288 Na_2SO_4 . $Na = 6.12$.

$C_{14}H_5O_5Cl_2SNa$ requires $Na = 6.07$ per cent.

When fused with potassium hydroxide and the product poured into water, a brilliant purple coloration is obtained.

1 : 4-Diphenoxyanthraquinone, $C_6H_2(OPh)_2 \begin{array}{c} \diagup CO \diagdown \\ \diagdown CO \diagup \end{array} C_6H_4$.

Ten grams of 1 : 4-dichloroanthraquinone were mixed with 15 grams of sodium hydroxide and a large excess of phenol, and the mixture heated in an oil-bath to 180° for two hours. The red liquid product was acidified, and the excess of phenol removed by distillation in a current of steam, when the diphenoxy-compound remained behind as a dark oily mass, which solidified on cooling. It crystallises from methyl alcohol in reddish-yellow needles, melting at 238° :

0.1676 gave 0.4875 CO_2 and 0.0621 H_2O . $C = 79.33$; $H = 4.1$.

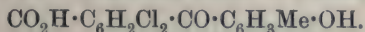
$C_{26}H_{16}O_4$ requires $C = 79.59$; $H = 4.05$ per cent.

1:4-*Diphenoxyanthraquinone* dissolves in concentrated sulphuric acid with a red colour, which changes to a rich amethyst on the addition of a little fuming sulphuric acid. When warmed on the water-bath with concentrated nitric acid containing a little fuming nitric acid it dissolves, forming a light red solution, from which, on pouring into water, a *dinitro*-derivative, melting at 206° , is precipitated.

0.1393 gave 7.1 c.c. N_2 at 17° and 746 mm. $N = 5.80$.

$C_{26}H_{14}O_8N_2$ requires $N = 5.81$ per cent.

3:6-*Dichloro-5'(or 6')-hydroxy-2-o(or m)-toluoylbenzoic Acid*,



3:6-Dichlorophthalic anhydride (180 grams), purified by distillation in a vacuum, was mixed with *p*-tolyl methyl ether (100 grams) in carbon disulphide solution, and aluminium chloride (300 grams) was gradually added. The mixture was heated on a water-bath for eight hours. The dark red semi-solid mass was then decomposed with ice and hydrochloric acid, and the carbon disulphide and the unchanged *p*-tolyl methyl ether were removed by distillation in a current of steam. The residual product was dissolved in sodium hydroxide, and again distilled in a current of steam with animal charcoal. The filtered alkaline liquid was decomposed by ice and hydrochloric acid, when the acid separated as a bulky, cream-coloured precipitate. It was collected, dried, and purified by crystallisation from acetic acid. Most of the 3:6-dichloromethoxy-2-toluoylbenzoic acid suffered hydrolysis, and some of the hydroxy-acid produced condenses to the quinone. By repeated crystallisation of the product of the reaction from methyl alcohol, 3:6-dichlorohydroxy-2-toluoylbenzoic acid was obtained, but it was somewhat difficult to free it from all traces of the methoxy-acid:

0.1428 gave 0.2914 CO_2 and 0.04524 H_2O . $C = 55.65$; $H = 3.53$.

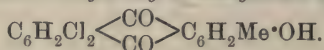
0.1635 „ 0.1468 $AgCl$. $Cl = 22.21$.

$C_{15}H_{10}O_4Cl_2$ requires $C = 55.38$; $H = 3.08$; $Cl = 21.84$ per cent.

3:6-*Dichloro-5'(or 6')-hydroxy-2-o(or m)-toluoylbenzoic acid* crystallises from methyl alcohol in colourless needles, melting at 173° . Its *sodium* salt is yellow. When heated with one molecular proportion of bromine in acetic acid solution on the water-bath, substitution readily occurs, and on pouring into water a *monobromo*-derivative is precipitated. It crystallises from methyl alcohol in pale yellow, minute needles, melting at 188° .

When warmed with sulphuric acid containing a little boric acid, it forms a quinone melting at 242° , but the yield is poor.

1 : 4-Dichloro-8-hydroxy-5-methylantraquinone,



This was prepared by heating the above 3 : 6-dichlorohydroxy-2-toluoylbenzoic acid with an excess of fuming sulphuric acid (containing 10 per cent. of sulphur trioxide) in presence of boric acid for a few minutes at 130°. The mixture was cooled, poured on ice, and filtered. It was freed from acid by boiling with sodium carbonate, washed with dilute hydrochloric acid, and crystallised from glacial acetic acid :

0.1231 gave 0.2662 CO₂ and 0.0321 H₂O. C = 58.97 ; H = 2.89.

0.1392 „ 0.1269 AgCl. Cl = 22.56.

C₁₅H₈O₅Cl₂ requires C = 58.63 ; H = 2.60 ; Cl = 23.12 per cent.

This quinone separates from acetic acid in minute, yellow needles, melting at 259°, and is sparingly soluble in benzene. It dissolves in concentrated sulphuric acid, giving a brilliant red solution with a purple fluorescence.

When 3 : 6-dichloromethoxy-2-toluoylbenzoic acid was condensed in a similar way, it was hydrolysed and gave the above quinone.

The *acetyl* derivative of 1 : 4-dichloro-8-hydroxy-5-methylantraquinone is readily prepared in the usual way by means of acetic anhydride and zinc chloride. It crystallises from acetic acid in long, lemon-yellow needles, melting at 181° :

0.1515 gave 0.3213 CO₂ and 0.0424 H₂O. C = 57.85 ; H = 3.11.

0.1297 „ 0.1080 AgCl. Cl = 20.68.

C₁₇H₁₀O₄Cl₂ requires C = 58.45 ; H = 2.86 ; Cl = 20.34 per cent.

1(or 4)-Chloro-8-hydroxy-4(or 1)-phenoxy-5-methylantraquinone.—

Unlike 1 : 4-dichloroanthraquinone, the chlorine atoms in the quinone derived from *p*-tolyl methyl ether are not replaced by heating with sodium phenoxide. In presence of copper powder, however, one chlorine atom is displaced by the phenoxy-group. 1 : 4-Dichloro-8-hydroxy-5-methylantraquinone (10 grams), phenol (50 grams), sodium hydroxide (20 grams), and copper powder (2 grams) are heated in an oil-bath at 180° for three hours. The brownish-red solution is acidified, distilled in a current of steam, and the residual oil left to solidify, any adhering oil being removed by porous porcelain. The quinone separates from methyl alcohol as a reddish-brown powder, melting at 268° :

0.1559 gave 0.3938 CO₂ and 0.0565 H₂O. C = 68.90 ; H = 4.02.

0.1003 „ 0.0410 AgCl. Cl = 10.01.

C₂₁H₁₃O₄Cl requires C = 69.14 ; H = 3.56 ; Cl = 9.74 per cent.

The compound is readily soluble in warm benzene or acetic acid, and dissolves in fuming sulphuric acid, forming a violet solution.

Attempts to prepare the corresponding phenylthiol derivative were unsuccessful.

3 : 6-Dichloro-3'(or 2')-hydroxy-2-o(or m)-toluoylbenzoic Acid,
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OH}.$

This acid was prepared by condensing 3 : 6-dichlorophthalic anhydride with *o*-tolyl methyl ether in presence of aluminium chloride, as described on p. 689. A reddish-purple product was obtained. After purification and recrystallisation from acetic acid, white needles, melting at 183° , separated :

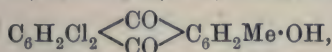
0.1473 gave 0.2977 CO_2 and 0.0475 H_2O . $\text{C} = 55.13$; $\text{H} = 3.59$.

0.1453 „ 0.1258 AgCl . $\text{Cl} = 21.87$.

$\text{C}_{15}\text{H}_{10}\text{O}_4\text{Cl}_2$ requires $\text{C} = 55.38$; $\text{H} = 3.08$; $\text{Cl} = 21.84$ per cent.

The properties of this acid are similar to those of 3 : 6-dichloro-5'(or 6')-hydroxy-2-*o*(or *m*)-toluoylbenzoic acid.

1 : 4-Dichloro-6(or 5)-hydroxy-5(or 6)-methylantraquinone,



was prepared in the same way as described on p. 690. The yield is slightly better than in the case of the corresponding 1 : 4-dichloro-8-hydroxy-5-methylantraquinone. The compound separates from acetic acid as a flocculent, yellow powder, which decomposes at 249° :

0.1063 gave 0.2313 CO_2 and 0.0313 H_2O . $\text{C} = 59.32$; $\text{H} = 3.27$.

0.1516 „ 0.1378 AgCl . $\text{Cl} = 22.49$.

$\text{C}_{15}\text{H}_8\text{O}_2\text{Cl}_2$ requires $\text{C} = 58.63$; $\text{H} = 2.60$; $\text{Cl} = 23.12$ per cent.

3 : 6-Dichloro-4'(or 2')-methoxy-2-o(or p)-toluoylbenzoic Acid,
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{OMe}.$

This acid was prepared as described on p. 689, but *m*-tolyl methyl ether was substituted for the para-compound. It separates from ether in colourless needles, melting at 212° , which are readily soluble in alcohol or acetic acid :

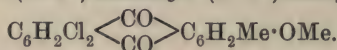
0.1694 gave 0.3531 CO_2 and 0.0596 H_2O . $\text{C} = 56.84$; $\text{H} = 3.85$.

0.1316 „ 0.1096 AgCl . $\text{Cl} = 20.60$.

$\text{C}_{16}\text{H}_{12}\text{O}_4\text{Cl}_2$ requires $\text{C} = 56.63$; $\text{H} = 3.54$; $\text{Cl} = 20.94$ per cent.

On fractionally crystallising from acetic acid, colourless, needle-shaped crystals separated, which decompose at 242° . This substance appears to be formed by the condensation of two molecules of *m*-tolyl methyl ether with one of 3 : 6-dichlorophthalic anhydride, but as only a small amount was isolated, it was impossible to obtain well-agreeing analyses.

1 : 4-Dichloro-7'(or 5'-)-methoxy-5'(or 7'-)-methylantraquinone,



This compound was obtained by condensing the acid described above in the usual way, but nearly all of it was sulphonated during the process, and a very small yield of the quinone was obtained. It is yellow, and, after crystallisation from acetic acid, decomposes at 236°.

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XLVI.—*The Absorption Spectra of the Vapours of Pyridine and Some of its Derivatives at Different Temperatures and Pressures.*

By JOHN EDWARD PURVIS.

THE absorption spectrum of the vapour of pyridine in a 1-dem. tube has been studied by Pauer (*Wied. Ann.*, 1897, **61**, 363), who observed bands at λ 2790, λ 2712, λ 2699, λ 2664, λ 2650, λ 2625, λ 2615, and then the rays from λ 2610 to λ 2350 were absorbed.

The aim of this investigation is to give an account of a series of observations of the spectra of the vapours of pyridine, α -picoline, 2 : 6-lutidine, 2 : 4-lutidine, 2 : 4 : 6-trimethylpyridine, and piperidine when observed under varying conditions of temperature and pressure. The ultimate object was to compare the influence on the bands in the substitution of hydrogen atoms by methyl groups in the pyridine nucleus, or the addition of hydrogen to the nucleus, as in piperidine.

The absorbing tube was similar, in principle, to that used by Pauer (*loc. cit.*), and also by Hartley (*Phil. Trans.*, 1908, *A*, **208**, 475) in his investigations of the absorption spectra of the vapours of benzene and its homologues. The tube used in the present investigations was 200 mm. long and 20 mm. in diameter. The ends were covered with quartz plates firmly attached by cemented screws. It was thereby made quite free from any leakage under the varying conditions of inside and outside pressures. There were two tubes attached to the absorption tube, one of which was connected to the small glass vessel containing the liquid the vapour of which was to be investigated, and the other with an aspirator.

The absorption tube was immersed in a rectangular bronze vessel, the two ends of which were fitted with quartz plates. The vessel was filled with distilled water, and heated from below in the series of observations at different temperatures and pressures.

In the first series of experiments air was aspirated through the liquid for a short time, so as to charge the absorption tube with the vapour at ordinary temperature and pressure. The connecting tubes were closed by pinchcocks placed very close to the orifices. After a photograph was taken of the spectrum of the vapour at the temperature and pressure of the laboratory, the temperature of the water was raised to 30° , and another photograph was taken. This operation was repeated at the higher temperatures of 45° , 60° , 75° , 90° , and the boiling point of water. Further, the pressure in the tube was observed by a gauge which registered the increased pressure.

In the second series of experiments, the observations were taken when the vapour was under reduced pressures and at two constant temperatures. The pinchcock on the inlet side was closed after the tube had been charged with the vapour. The vapour pressure was reduced by a pump, and a photograph taken of the absorption spectrum. The pinchcock on the inlet side of the tube was then opened so as to allow the air to aspirate through the liquid and until the mercury column of the gauge descended to a definite height. The operation was repeated at different pressures, until the pressure of the atmosphere was reached.

In the whole series of experiments, therefore, the absorption spectra of a constant amount of vapour was investigated (1) at increased temperatures and pressures, and (2) at two constant temperatures and decreased pressures.

The condensed cadmium spark was used as the source of the continuous rays, and the plates were exposed for five minutes for each observation. The spectroscope was made by Hilger. It has a scale of wave-lengths which can be photographed on the plate, and the positions of the bands can be determined quite easily. In addition to this, and to confirm the accuracy, the bands of the earlier plates were measured by a Zeiss comparator, using the Cd lines as fiducial lines.

The pyridine, α -picoline, and 2:4:6-trimethylpyridine were kindly placed at my disposal by Dr. W. J. Sell, and they were redistilled before use. The two lutidines and the piperidine were repeatedly distilled. The 2:6-lutidine boiled at 140 – 142° , the 2:4-lutidine boiled at 155° , and the piperidine at 105 – 106° ; pyridine boiled at about 114° , α -picoline at about 120° , and 2:4:6-trimethylpyridine at about 170° .

Pyridine.

TABLE I.

The absorption bands in pyridine vapour at various temperatures and pressures in a column 200 mm. long. Barometric pressure = 758 mm.

Abbreviations: sh. = sharp; v.w. = very weak; narr. = narrow; diff. = diffuse; r.w. = rather weak; m.w. = moderately wide; w. = weak; str. = strong; m.str. = moderately strong; f.sh. = fairly sharp.

14°.	30°.	45°.	60°.	
758 mm.	802 mm.	828 mm.	858 mm.	
λ.	λ.	λ.	λ.	
2878 v.w., sh.	2877 w., f.sh.	2877 w., f.sh.	2930 v.w., narr.	
2869 " "	2869 v.w., f.sh.	2868 v.w., narr.	2918 " "	
2866 " "	2866 w., f.sh.	2866 " "	2913 " "	
{ 2861 v.w., narr.	{ 2861 v.w., narr.	{ 2861 " "	{ 2895 " "	
{ 2859 " "	{ 2859 " "	{ 2859 " "	{ 2892 " "	
2855 v.w.	2855 " "	2855 " wide	2878 str., narr.	
{ 2849 " "	{ 2849 " "	{ 2849 " "	2870 v.w., narr.	
{ 2843 " "	{ 2843 " "	{ 2843 " "	2866 m.str., narr.	
2832 str., sh.	2832 str., f.sh.	2832 str., m.w.	{ 2862 v.w., narr.	
2822 v.w., sh.	2821 v.w., sh.	2822 w., f.sh.	{ 2860 " "	
2815 diff., wide	2814 w., diff.	2815 diff., wide, w.	2855 " "	
2809 " "	2809 " "	2809 " "	{ 2850 wide	
2806 v.w.	2806 v.w.	2806 f.str., narr.	{ 2845 diff., w.	
2798 " narr.	2798 " narr.	2798 v.w., narr.	2832 v.str., wide	
2796 " diff.	2796 " diff.	2796 m.str., narr.	2822 w., diff.	
2795 " "	2794 " narr.	2794 v.w., narr.	2816 v.wide, diff.	
2789 str., sh.	2788 str., f.wide	2788 str., m.wide	2809 w., diff.	
2784 v.w., narr.	2784 v.w., narr.	2785 w., narr.	2806 str., wide, diff.	
{ 2782 " "	{ 2782 " "	{ 2782 " "	2796 m.str., narr.	
{ 2778 " "	{ 2778 " "	{ 2778 " "	2795 " "	
2762 " "	2762 " "	2762 v.w., narr.	2788 str., wide	
{ 2760 " "	{ 2760 " "	{ 2760 " "	2785 v.w., narr.	
{ 2758 " "	{ 2758 " "	{ 2758 " "	{ 2783 " "	
2754 str., narr.	2754 f.str., sh.	2753 v.str., sh.	{ 2778 w., narr.	
{ 2747 v.w., narr.	{ 2746 w., f.sh.	{ 2746 w., narr.	2775 v.w.	
{ 2743 " wide	{ 2743 " "	{ 2744 " "	{ 2759 v.w., wide	
{ 2738 v.w., m.w.	{ 2738 w., wide	2739 v.w., m.wide	{ 2758 " "	
{ 2736 " "	{ 2736 " "		2753 m.str.	
2733 " narr.	2732 v.w., narr.	From λ 2735 there was almost complete absorption of rays, only the strong Cd line λ 2194 and λ 2144 being just visible.	2750 general absorption began.	
2730 str., wide	2729 f.str., wide			
2726 " "	2724 m.str.			
2718 w., m.w.	2719 v.w., wide			
2713 m str., wide	2712 " "			
{ 2696 diff., w.	From λ 2700 to the Cd line 2265 there was a strong absorption and then the rays beyond came through.			
{ 2690 " "				
{ 2685 " "				
2678 w., narr.				
2673 w., diff.				

From λ 2660 there

From λ 2660 there was a strong absorption of rays to the strong Cd λ 2329, and then all the rays beyond came through.

33 bands

33 bands

27 bands

28 bands

TABLE I (*continued*).

75°.	90°.	100°.
888 mm.	918 mm.	934 mm.
λ .	λ .	λ .
2929 v.w., narr.	2929 w., f.sh.	2930 v.w., sh.
2918 „ wide	2920 v.w., narr.	2920 „ „
2912 „ diff.	2917 „ „	2918 „ „
2909 „	2913 „ „	2912 „ narr.
{ 2895 „	2908 „ „	2908 „ diff.
{ 2892 „	{ 2895 „ narr.	{ 2895 „
2878 str., narr.	{ 2892 „ „	{ 2892 „
2872 v.w.	2878 str.	2879 str., narr.
2869 „ narr.	2872 v.w., narr.	2872 v.w., narr.
2866 str., wide	2869 „ „	2869 „ „
{ 2861 v.w., narr.	2866 str., sh.	2866 str., sh.
{ 2860 „ „	{ 2862 v.w., narr.	{ 2862 v.w., narr.
2855 „ wide, diff.	{ 2859 „ „	{ 2860 „ „
2849 „ m.wide	2855 „ „	2855 „ wide
2845 „ narr.	2849 „ wide	2850 w., wide
2843 „ „	2846 „ „	2846 w.
2842 „ „	2845 „ „	2844 w.
2832 str., wide	2842 „ narr.	2843 w., narr.
2822 mod., str.	2832 str., wide	2833 f.str., wide
2815 v.wide, v.diff.	2822 w., wide	2823 w., wide
2809 w.diff.	2816 „ „	2816 v.w., diff.
2806 f.str., wide	2809 „ „	2800 general absorption
2796 w.diff.	2800 general absorption	begins.
2795 „	begins.	
2788 diff., weak		
*2780 w., wide, diff.		
2770 general absorption		
begins.		

26 bands

22 bands

21 bands

* λ 2782 and λ 2778 diffuse into each other with increased temperature and pressure, and the centre of the band was then λ 2780.

On comparing the photographs taken under the conditions of varying temperatures and pressures, it was quite evident that the bands on the less refrangible side, which were very faint or just visible, became stronger and better marked as the temperature and pressure increased. Moreover, all the bands became stronger and wider as the temperature and pressure increased. At the same time the general absorption increased, so that a number of bands on the more refrangible side were obliterated; the general effect being that, as the temperature and pressure increased, the bands were widened: more bands appeared on the less refrangible side: the general absorption increased; and some of the bands on the more refrangible side disappeared. Further, on the more refrangible side, there appeared to be indications of a very strong band, for at 14° and 758 mm. pressure the rays were absorbed from about λ 2660 to the Cd 2329, and this band gradually became wider with increasing temperature and pressure, so that at 45° and 828 mm. pressure it was almost wholly obliterated by the increased

general absorption, and at 60° and 858 mm. pressure the band disappeared.

An attempt has been made to arrange the pyridine bands in some sort of order, and it will be seen from the following table that there appears to be a definite regular arrangement of the majority of the bands. There is a difference in their wave-lengths which assumes a fairly consistent regularity when the bands are arranged in groups. It is most probable that with greater dispersion, and the consequent more exact measurements, these differences would be less marked.

2930								
64 ?	2918							
2866	56	2913						
57	2862	53	2909					
2809	56	2860	54	2895				
51	2806	62	2855	52	2892			
2758	52	2798	59	2843	60	2878		
62	2754	51	2796	54	2832	56	2872	
2696	64	2747	53	2789	54	2822	57	
	2690	62	2743	51	2778	60	2815	
		2685	65	2738	52	2762	55	
			2678	65	2726	49	2760	
				2673		2713		

Besides this regularity observed from a consideration of the whole of the bands, there are various small groups which are related. The general appearance of these bands is that the intensities of the groups increase as the wave-lengths increase, and, also, that the first member of each group is the strongest, the second member is not quite so strong, and the third member is a little stronger and more diffuse than the second. The following is the arrangement of these groups of triplets, with their differences in Ångström units:

2930	2878	2832	2789	2754
12	12	10	11	11
2918	2866	2822	2778	2743
9	11	12	16 ?	13
2909	2855	2809	2762	2730

If the corresponding members of each of these groups are arranged in tabular form, the following differences are observed:

2930	52	2918	52	2909	54
2878	46	2866	44	2855	46
2832	43	2822	44	2809	47
2789	35	2778	35	2762	32
2754		2743		2730	

Further, some of the bands are closely related doublets. These bands are equally strong, and the differences of their wave-lengths differ by about two units only. Such bands are:

2861	2781	2760	2746	2739
2859	2779	2758	2743	2737
>2	>2	>2	>3	>2

TABLE II.

The absorption bands in pyridine vapour at a constant temperature of 15° and at different pressures. Barometric pressure = 758 mm.

Abbreviations: str.=strong; narr.=narrow; v.w.=very weak; w.=weak; f.str.=fairly strong; v.narr.=very narrow; sh.=sharp; f.sh.=fairly sharp; mod.wide=moderately wide; v.str.=very strong; m.w.=moderately weak; diff.=diffuse.

758 mm.	628 mm.	478 mm.
λ.	λ.	λ.
2879 str., narr.	2878 f.str., narr.	2879 f.str., sh.
2869 w., narr.	2869 w., narr.	2869 sh., w.
2866 f.str., sh.	2867 w., f.str.	2866 f.str., sh.
2861 v.w., narr.	2861 v.w., narr.	2860 v.w., narr.
2860 w., narr.	2859 " "	2850 f.str., narr.
2855 w., mod.wide	2854 " "	2843 str., sh.
2850 f.str., wide	2849 f.str., narr.	2832 " "
2845 " "	2845 v.w., wide	2822 f.str., sh.
2832 v.str., narr.	2832 str., narr.	2815 v.w., wide
2822 str., narr.	2821 f.str., narr.	2809 " narr.
2815 v.w., wide	2815 v.w., wide	2807 " "
2809 w., v.narr.	2809 " narr.	2800 w., wide, sh.
2807 narr., v.w.	2807 " "	2797 f.str., sh.
2799 f.str., narr.	2799 w., narr.	2795 v.w., sh.
2796 str., narr.	2796 f.str., narr.	2789 str., sh.
2795 w., narr.	2795 w., narr.	2785 v.w., sh.
2789 str., narr.	2788 str., narr.	2782 " "
2785 w., narr.	2785 w., narr.	2779 " "
2781 " "	2781 " "	2762 " narr.
2779 " "	2799 " "	2760 " sh.
2762 v.w., narr.	2762 v.w., narr.	2758 " "
2760 w., narr.	2760 w., narr.	2756 " "
2758 " "	2758 " "	2754 f.str., sh.
2753 str., narr.	2755 v.w.	2747 " "
2746 w., narr.	2753 str., narr.	2743 " "
2743 " "	2746 f.str., narr.	2740 w., f.wide
2739 w., m.wide	2743 " "	2735 f.str., narr.
2737 w., wide	2739 " "	2733 w.
2733 " "	2735 " "	2730 f.str., narr.
2730 " "	2733 w., wide	2725 " "
2727 " "	2730 str., wide	2719 w., narr.
	2725 m.w., wide	2712 f.wide, w.
	2718 m.w., v.w.	2705 w., narr.
	2712 w., wide	2690 v.w., wide

From λ 2720 to the Cd line 2329 there was a strong absorption of rays, and then the rays beyond were transmitted. The Cd 2329 is just visible.

From λ 2700 to the Cd line 2329 there was strong absorption; the line 2329 was much stronger than at the pressure of 758 mm.; and then the rays beyond were transmitted.

From λ 2680 to the Cd line 2329 the rays were absorbed, although the strong Cd line 2573 was just visible.

TABLE II (*continued*).

328 mm.	178 mm.	28.5 mm.
λ .	λ .	λ .
2879 f.str., sh.	2879 f.w., narr.	2878 v.w.
2870 w., narr.	2870 v.w., narr., diff.	2869 "
2866 " "	2866 w., narr.	2867 "
2860 v.w., narr.	2833 f.str., diff.	2833 w.
2850 " "	2822 f.str., narr.	2822 "
2833 str., sh.	2799 v.w., v.narr.	2799 v.w.
2821 w., sh.	2796 w., v.narr.	2796 "
2809 v.w., sh.	2789 f.str., narr.	2789 " narr.
2806 " "	2762 v.w.	2695 " "
2799 " narr.	2760 " v.narr.	2690 " "
2796 f.str., diff.	2759 " "	2686 " "
2789 str., f.sh.	2753 f.str., v.narr.	2675 " "
2785 v.w., sh.	2730 " wide	
2781 " "	2725 " "	
2779 " "	2719 w., narr., diff.	
2762 " narr.	2712 f.str., wide, diff.	
2760 " "	2705 v.w., narr.	
2759 " "	2695 f.wide, w.	
2756 " "	2690 " " "	
2753 f.str., sh.	2686 " diff.	
2746 v.w., sh.	2672 w., diff.	
2743 " f.sh.		
2740 " "		
2736 " "		
2733 w.		
2730 f.str., wide		
2725 " "		
2719 w., wide		
2712 f.str., f.sh.		
2705 w., sh.		
2695 w., wide		
2690 " "		
2686 " "		
2681 " "		
2672 " "		

All the rays were transmitted beyond λ 2675.

All the rays were transmitted beyond λ 2672, although the continuous spectrum was weak between λ 2550 and λ 2400.

From λ 2665 to λ 2350 there was strong absorption, and the Cd line 2573 was much stronger than at the pressure of 478 mm.

35 bands

21 bands

12 bands

The effect of reducing the pressure is to lessen the amount of vapour, with the consequent disappearance of the less intense bands, so that, at the lowest pressure of 28.5 mm., even the strongest bands are weak, and the bands become sharper and narrower.

On comparing the first column of wave-lengths with that of table I, it will be noticed that a difference of 1° has produced, at the higher temperature of 15° , an obliteration of the bands λ 2718 to λ 2673, and has shifted the region of general absorption from the region of λ 2660 to λ 2770.

On decreasing the pressure, at first the effect has been to produce

more bands on the more refrangible side, and then, as the amount of vapour in the tube lessened, the number of bands decreased, the strongest bands only remaining visible at the lowest pressure.

TABLE III.

The absorption bands in pyridine vapour at a constant temperature of 100° and at different pressures. Barometric pressure = 764 mm.

Abbreviations: str.=strong; sh.=sharp; w.=weak; v.w.=very weak; diff.=diffuse; narr.=narrow; f.str.=fairly strong.

764 mm.	604 mm.	511 mm.	429 mm.
λ .	λ .	λ .	λ .
2879 str., sh.	2881 w., v.narr.	2882 v.w.	2881 v.w.
2869 w., v.narr.	2871 " "	2871	2837 " diff.
2866 " "	2869 " "	2869	2825 " "
2861 w., narr.	2865 " "	2857	2791 v.w.
2860 " "	2862 " "	2832 f.str., diff.	
2855 " "	2857 " "	2825 w., diff.	From λ 2650 all the rays came through, although they were very weak between Cd 2329 and 2573.
2850 f.str., narr.	2852 " "	2789 w., narr.	
2847 v.w.	2847 } only traces	2755 v.w.	
2845 " "	2845 } visible		
2832 str., diff.	2832 str., diff.	From λ 2700 to Cd	
2822 " "	2823 " "	2329, which was	
2815 v.w., wide	2815 v.w.	much stronger than	
2809 " "	2809 " "	at 429 mm. pressure,	
2800 wide, w.	2801 diff., wide	there was absorption,	
2796 " "	2796 w., diff.	and then the rays	
2789 " "	2789 f.str.	beyond were trans-	
2770 general ab-	2755 " "	mitted.	
sorption, although	2747 w., narr.		
there was a very weak	2745 " "		
image of Cd 2265.			

From λ 2730 to Cd 2329, which was weak, there was absorption, and then beyond this the rays were transmitted.

16 bands	19 bands	8 bands	4 bands
339 mm.	354 mm.		169 mm.
λ .	λ .		89 "
2833 v.w.	2433 v.w.		30 "
2823 "			
2791 "			
And then all the rays transmitted fairly strongly.	All the rays were transmitted with the above exception.		At these pressures no bands were seen; all the rays were transmitted.

3 bands

1 band

No bands

At the temperature of 100° , therefore, and by decreasing the pressure, the bands rapidly disappeared. If the first column of table II is compared with the first column of the above table, it will be seen that the effect of the increased temperature has been

to obliterate all the bands on the more refrangible side of λ 2789, and to shift the region of general absorption towards the red end, and then to increase slightly the number of bands when the pressure was reduced to 604 mm. After that, as the amount of vapour in the tube diminished, the number of bands rapidly diminished, and the region of general absorption was shifted towards the more refrangible end. Finally, at the lowest pressures, all the rays were transmitted, and the bands disappeared.

α -Picoline.

TABLE IV.

The absorption bands of α -picoline vapour at various temperatures and pressures in a column 200 mm. long. Barometric pressure = 745 mm.

Abbreviations: v.w. = very weak; sh. = sharp; narr. = narrow; f.w. = fairly wide.

15°.	30°.	45°.	60°.
745 mm.	789 mm.	815 mm.	845 mm.
λ .	λ .	λ .	λ .
2880 v.w., sh.	2880 v.w., sh.	2879 v.w., narr.	2880 v.w.
2861 „ narr.	2861 „ narr.	2861 „ „	2861 „ narr.
2859 „ „	2859 „ „	2859 „ „	2859 „ „
2856 „ „	2856 „ „	2855 „ „	2856 „ „
2846 „ wide	*2853	2853	2853
2834 sh., narr.	2846 w., wide	2845 w., wide	2845 v.w.
2821 v.w., narr.	2834 sh., narr.	2833 w., narr.	2833 w., sh.
2819 „ „	2819 v.w., narr.	2790 general ab-	2800 general ab-
2814 w., wide	2814 w., wide	sorption began, the	sorption began, the
2809 wide	2809 wide	Cd 2748 being vis-	Cd 2748 being just
2790 w., narr.	2790 w., f.wide	ible.	visible.
2786 w., wide	2785 „ „		
2785 „ „			
2781 v.w.	From λ 2770 to Cd		
	2265 there was a		
From λ 2750 to Cd	strong absorption of		
2329 the rays were	the rays, the line		
strongly absorbed;	2194 being just vis-		
the rays $\lambda\lambda$ 2313,	ible.		
2288, 2265, 2194,			
2144 being just	* Head of broad		
visible.	band diffuse towards		
	violet end.		
14 bands	13 bands	7 bands	
75°.	90°.	100°.	
875 mm.	905 mm.	921 mm.	
λ .	λ .	λ .	
2880 sh., narr.	2880 sh., narr.	2880 sh., narr.	
2834 „ „	2840 general absorp-	2840 general absorp-	
2820 general absorp-	tion began, Cd 2837	tion, Cd 2837 ending it	
tion began.	ending it sharply.	sharply.	
2 bands	1 band	1 band	

It will be seen from table IV that the number of bands was considerably less than was found in the pyridine vapour. Besides that there was a shift towards the red end of the general absorption. The two series of observations indicate that the weighting of the molecule of pyridine by the introduction of a methyl group has had a profound influence on the vibrations of the molecules. Comparing the bands in more detail, it will be seen that when the temperature and pressure were increased, there was no appearance of the series of bands λ 2930, λ 2918, λ 2913, λ 2895, λ 2892, which were noted in the spectra of pyridine vapour at corresponding temperatures and pressures. There was no appearance of the bands λ 2869, λ 2866; the two pyridine bands λ 2849, λ 2843 widened into one band at λ 2846; a new band appeared at λ 2819. There were no bands corresponding with the bands λ 2806, λ 2798, λ 2796, λ 2795. The following table compares the bands of pyridine and α -picoline common to the two substances observed at practically the same temperature and pressure:

Pyridine.	α -Picoline.	Pyridine.	α -Picoline.
2878	2880	2822	2821
2861	2861	2815	2814
2859	2859	2809	2809
2855	2856	2789	2790
{ 2849	2846	2784	2785
{ 2843		2782	2781
2832	2834		

It will be seen that, although some of the bands of pyridine within this region are absent in α -picoline, there is a close agreement between those which are present.

The general effect, therefore, of the introduction of the methyl group has been (1) to obliterate a considerable number of the bands found in pyridine, and (2) to shift the region of general absorption more towards the red end of the spectrum.

A series of observations were made of the spectra of α -picoline vapour at two constant temperatures of 13° and 100° , and at gradually reduced pressures. No new bands appeared, and as the pressure was reduced, these rapidly disappeared, so much so that, at 100° , no bands were seen. The following tables describe the positions of general absorption at the various pressures.

TABLE V.

The absorption spectrum of α -picoline at a constant temperature of 13° and at different pressures.

Abbreviations: w. = weak; v.w. = very weak.

633 mm.	483 mm.	333 mm.
λ .	λ .	λ .
2789 w.	2789 w.	2789 v.w.
Absorption of rays from λ 2700 to Cd 2329, and then the rays were transmitted. Cd 2329 is weak.	Absorption of rays from λ 2690 to about λ 2350.	Absorption of rays from λ 2670 to λ 2380, Cd 2573 being just visible.
183 mm.		33 mm.
λ .		No band visible.
2789 v.w.		
Almost complete transmission of rays, the Cd lines between 2573 and 2329 being well marked.		Continuous transmission of rays well marked throughout; although they were weakest from about λ 2550 to λ 2500.

TABLE VI.

The absorption spectrum of α -picoline at a constant temperature of 100° and at different pressures.

763 mm.	633 mm.	483 mm.
General absorption from λ 2770, although Cd 2748 was just visible.	General absorption from λ 2750, although Cd 2194 and 2144 were just visible.	General absorption ends sharply at Cd 2748, and then Cd 2321, 2313, 2265, and 2194 were just visible.
333 mm.	183 mm.	33 mm.
General absorption just beyond Cd 2748, which was very strong. The Cd lines beyond this in the ultra-violet were visible.	Strong absorption of rays from λ 2710 to λ 2340, and then the Cd lines beyond this were strongly marked.	Strong absorption of rays from λ 2660 to λ 2400, but Cd 2573 was also well marked. Beyond λ 2400 the rays were transmitted.

The tables show that, precisely as in pyridine, the increased temperature produced a rapid disappearance of the bands; and that, as compared with the observations at the lower temperature of 13° (table V), the position of general absorption was shifted more towards the red end of the spectrum.

2: 6-Lutidine.

Photographs of the absorption spectra of 2: 6-lutidine were also taken, and the following notes describe the phenomena observed.

At 12° and 737 mm. pressure.—No narrow bands were observed comparable with those of pyridine or α -picoline, but there was a strong absorption of rays between λ 2710 to λ 2350; and after this the series of Cd lines from λ 2329 to λ 2144 were well marked, and there was a faint appearance of λ 2573.

At 30° and 781 mm. pressure.—There was an absorption of the rays from λ 2750 to λ 2329, and then the Cd lines were weaker than at 12°; Cd 2144 was quite obliterated.

At 45° and 807 mm. pressure.—Absorption of rays from λ 2760 to λ 2310; the Cd lines 2313 and 2265 were just visible.

At 60° and 837 mm. pressure.—General absorption commenced at λ 2780, and all the Cd lines had disappeared.

At 75° and 867 mm. pressure.—General absorption commenced at λ 2800.

At 90° and 897 mm. pressure.—General absorption commenced at λ 2815.

At 100° and 913 mm. pressure.—General absorption commenced at λ 2830.

It is evident that no lines or bands were observed in the vapour of 2: 6-lutidine comparable with those of pyridine or α -picoline. The presence of two methyl groups in the molecule obliterated such bands. On the other hand, there were strong indications of a very strong band comparable with a similar band in both pyridine and α -picoline, but its position was moved more towards the red end of the spectrum; and, as in the case of the two latter substances, this band disappeared under the increased general absorption as the temperature and pressure were increased.

2: 4-Lutidine.

The isomeric 2: 4-lutidine spectra were also observed, and the following notes describe the phenomena observed.

At 12° and 737 mm. pressure.—The rays were all transmitted to Cd 2144 with no appearance of bands.

At 30° and 781 mm. pressure.—The rays were transmitted to Cd 2144, the latter being weak.

At 45° and 807 mm. pressure.—The rays were transmitted to Cd 2144, the latter being just visible.

At 60° and 837 mm. pressure.—There was an absorption of rays between λ 2640 and λ 2380, although the Cd lines 2573, 2472, and 2420 were well marked; the Cd lines 2329 to 2194 were strongly marked.

At 75° and 867 mm. pressure.—There was an absorption of rays between λ 2690 and λ 2330; the Cd line 2572 was very weak; the Cd lines from λ 2329 to λ 2265 were fairly strong, and Cd 2194 was only just visible.

At 90° and 897 mm. pressure.—There was a sharp absorption of rays from Cd 2750 to Cd 2329. The Cd lines 2329, 2321, 2313, 2285, 2265 were weak; Cd 2194 was just visible.

At 100° and 913 mm. pressure.—There was an absorption of

rays from λ 2750 and ending at λ 2329; the Cd lines from λ 2329 to λ 2265 were weak.

The above observations, therefore, indicate that, as in 2: 6-lutidine, there were no narrow bands in the vapour comparable with those of pyridine and α -picoline, but there was a strong band not unlike that found in 2: 6-lutidine.

2: 4: 6-Trimethylpyridine.

The absorption spectra of 2: 4: 6-trimethylpyridine were observed, and the following notes describe the observed phenomena.

At 16° and 748 mm. pressure.—The rays were transmitted strongly to about λ 2700, and then the continuous spectrum was absent to about λ 2550, although the lines λ 2677 and λ 2573 were well marked. From λ 2550 the continuous spectrum was well marked up to 2194, the Cd lines 2329, 2321, 2313, 2288, 2265, and 2239 being quite strong.

At 30° and 792 mm. pressure.—The rays were absorbed from λ 2720 to about λ 2380, the Cd 2573 being very weak. The Cd lines 2329, 2321, 2313, 2288, 2265 were strong, whilst 2194 was very weak.

At 45° and 818 mm. pressure.—The rays were absorbed from λ 2730 to Cd 2329, which was sharp and fairly strong, and the Cd lines beyond to λ 2265 were still strong; the line λ 2239 was just visible.

At 60° and 848 mm. pressure.—The rays were absorbed from the Cd lines 2748, which was sharp on the more refrangible edge, to Cd 2329, which was weak. The Cd lines to 2265 were fairly strong, and, beyond, there was complete absorption.

At 75° and 878 mm. pressure.—The rays were absorbed from Cd 2750 to Cd 2329, which was just visible. The Cd lines beyond to λ 2265 were very weak.

At 90° and 908 mm. pressure.—The rays were absorbed from λ 2760 to Cd 2321. The Cd line 2329 had disappeared; the Cd lines 2321, 2313, 2284, 2265 were just visible.

The absorption spectrum of trimethylpyridine shows that the vapour, like that of the two lutidines, has no bands comparable with those of pyridine or α -picoline. On the other hand, it does possess one large band, which is shifted more towards the red end of the spectrum, when the numbers are compared with those of the lutidines, and with those of pyridine and α -picoline. The presence of this large band is common to all the substances examined, whilst pyridine and α -picoline are the only two substances which possess a series of narrow bands.

Piperidine.

TABLE VII.

The absorption bands in piperidine vapour at various temperatures and pressures in a column 200 mm. long. Barometric pressure=763 mm.

Abbreviations: v.w.=very weak; narr.=narrow; w.=weak; sh.=sharp; str.=strong; m.str.=moderately strong; m.wide=moderately wide.

15°.	30°.	45°.
762 mm.	807 mm.	833 mm.
λ.	λ.	λ.
2637 v.w.	2628 w., wide	2631 v.w., narr.
2633 "	2625 w.	2630 " "
2628 "	2605 v.w., wide	2628 " stronger and
2625 "	2600 " "	wider than 2630
2599 " narr.	{ 2596 " narr.	or 2631
{ 2596 " "	{ 2594 " "	2624 v.w.
{ 2595 " "	{ 2590 " "	2618 " wide
{ 2591 w., narr.	{ 2588 str., "	2613 " "
{ 2590 " "	{ 2587 w., wide	2605 " "
{ 2589 " but stronger	{ 2585 " "	2600 " "
than 2591	{ 2579 str., wide	2595 " "
2586 w., narr.	2576 w., narr.	{ 2591 w., narr.
2579 sh., narr.	2570 " "	{ 2589 " "
2565 w., wide	2565 str., wide	{ 2587 v.w., narr.
2558 v.w., wide	2558 m.str., wide	{ 2585 " "
{ 2552 " narr.	{ 2551 w., narr.	{ 2581 str., narr.
{ 2550 " "	{ 2550 " "	{ 2579 " "
2547 " "	2547 " "	2576 " "
2543 " wide	2543 w., wide	2570 " "
{ 2539 f.str.	2539 str., wide	2567 v.w., narr.
{ 2535 str., wide	2535 " "	2564 str., wide
{ 2530 " "	2530 " "	2558 " "
2528 v.w., narr.	2527 w., narr.	{ 2551 w., narr.
{ 2526 w., narr.	{ 2526 " "	{ 2550 " "
{ 2521 " "	{ 2521 " "	2546 w., wide
{ 2519 str., wide	{ 2519 str., wide	2542 v.w., wide
{ 2513 " "	{ 2513 " "	2538 " "
{ 2507 " "	{ 2507 " "	2535 " "
2503 " narr.	2502 w., wide	2530 " "
2502 w., wide	2499 w., narr.	
{ 2499 w., narr.	2495 " "	
{ 2495 " "	2490 " "	
2490 " "		
2472 " "		
2467 " "		
{ 2461 w., wide		
{ 2455 " "		
{ 2450 " "		

General absorption began at about λ 2520.

General absorption began at about λ 2485, although the Cd lines at 2321 and 2313 were just visible.

General absorption began at about λ 2440, although there was a transmission of rays beyond, the Cd lines 2329, 2321, and 2313 being visible.

TABLE VII (*continued*).

60°.	75°.	90°.	100°.
863 mm.	893 mm.	923 mm.	939 mm.
λ .	λ .	λ .	
2656 v.w.	2656 v.w., narr.	*2630 v.w.	No bands visible.
2655 "	2655 " "	2628 "	
{ 2631 " narr.	{ 2650 " "	2623 " wide	General absorption
{ 2629 " "	{ 2647 " "	2618 "	began at λ 2630.
{ 2628 " "	{ 2645 " "		
2624 w., wide	{ 2631 " "	General absorption	
2618 " "	{ 2629 " "	began at about	
2613 " "	{ 2627 " "	λ 2610.	
2605 v.w., wide	2623 m.str., wide		
2600 w., m.wide	2618 v.w., wide	* λ 2631 and λ 2629	
2595 w., wide	2613 " "	widen into λ 2630	
{ 2591 w., narr.	2605 " "	by increased tem-	
{ 2589 " "	2599 " "	perature and pres-	
*2585 w., wide	2595 " "	sure.	
2581 str., narr.	{ 2590 "		
2579 str., m.wide	{ 2588 "		
2576 " "	2590 and 2588 al-		
2570 m.wide	most widen into		
2567 v.w., narr.	each other by		
2563 " m.wide	increased tem-		
2558 " "	perature and		
	pressure.		
General absorption	2585 v.w., wide		
began at about	2580 "		
λ 2550.	2578 "		
	2580 and 2578 al-		
* λ 2587 and λ 2585	most widen into		
widen into each	each other by		
other by increase	increased tem-		
of temperature and	perature and		
pressure.	pressure.		
	2574 f.str., wide		
	2570 v.w., wide		
	General absorption		
	began at about		
	λ 2565.		
21 bands	21 bands	4 bands	No bands

On comparing the piperidine bands with those of pyridine, the differences in their appearances were quite clear. The piperidine bands were wider and more diffuse; they had not the sharp, well-defined appearance characteristic of the pyridine spectrum. They were also different from those of benzene, although some of them were almost coincident as regards their wave-lengths. The absorption spectrum of benzene vapour was examined under the same conditions, and the two series of spectra were compared. The benzene bands were largely bands having their sharpest edges on the less refrangible side, whereas the piperidine bands generally were much wider, and were equally diffuse on each side. Further,

the strong bands of benzene between λ 2650 and λ 2700 were absent in the piperidine vapour.

It will be noticed that, as in pyridine, more bands on the less refrangible side became visible under the conditions of increased temperature and pressure; and that the general absorption was shifted towards the less refrangible side, so much so that at 100° and 939 mm. pressure no bands were seen.

It is also noticeable that the positions of the piperidine bands were not in the direction of less refrangibility, although the weight of piperidine is greater than that of pyridine. The general absorption in the two substances shows similar differences; the region where general absorption began in piperidine vapour was more towards a position of greater refrangibility.

The majority of the bands show some regular relationship in their periods of vibrations, for if the bands are arranged in series, as in pyridine, the following differences are observed:

2637			2599				2565			
94	2638		66	2596			58	2558		
2543	94	2628	2633	68	2591		2507	59	2552	
	2539	93	2625	2528	65	2586		2499	57	2547
		2535	95		2526	65	2579		2495	57
			2530			2521	66			2490
							2513			

Further, there are a series of wide, somewhat diffuse bands which are very similar in their general appearance, and which occur in groups of three. These are:

2595	2539	2519	2499	2461
5	4	6	4	6
2590	2535	2513	2495	2455
4	5	6	5	5
2586	2530	2507	2490	2450

If the corresponding numbers of these triplets are compared, there is the following relationship between them:

2595	2590	2586
56	55	56
2539	2535	2530
20	22	23
2519	2513	2507
20	18	17
2499	2495	2490
38	40	40
2461	2455	2450

TABLE VIII.

The absorption bands in piperidine vapour at a constant temperature of 17.5° and at different pressures. Barometric pressure = 756.

Abbreviations: w.=weak; narr.=narrow; m.wide=moderately wide; v.w.=very weak; m.w.=moderately weak.

626 mm.	476 mm.	326 mm.
λ .	λ .	λ .
2577 w., narr.	2577 w., narr.	2577 v.w., narr.
2549 w., wide	2550 w., wide	2549 " wide
2545 w., narr.	2545 w., narr.	2545 " narr.
2541 w., m.wide	2541 v.w., wide	2542 w., wide
{ 2539 m.w., wide	{ 2539 " "	{ 2539 m.w., wide
{ 2534 " "	{ 2535 " "	{ 2534 " "
{ 2530 " "	{ 2531 m.w., wide	{ 2530 " "
{ 2529 m. narr.	{ 2529 w., narr.	{ 2528 " "
2525 w., narr.	2527 w., wide	2525 w., narr.
{ 2522 " "	2524 w., narr.	{ 2523 " "
{ 2520 " "	{ 2521 " "	{ 2521 " "
{ 2518 narr.	{ 2520 " "	{ 2517 " "
{ 2515 " "	{ 2516 m.w., wide	{ 2512 " "
{ 2512 w., wide	{ 2512 " "	{ 2506 " "
{ 2506 " "	{ 2506 " "	{ 2500 " "
{ 2500 m.w., wide	{ 2500 " "	{ 2498 " "
{ 2495 " "	{ 2495 " "	{ 2495 " "
{ 2489 " "	{ 2489 " "	{ 2489 " "
{ 2460 w., wide	{ 2460 " "	{ 2460 " "
{ 2455 " "	{ 2455 " "	{ 2455 " "
{ 2450 " "	{ 2449 " "	{ 2449 " "
		2442 " "

The rays were absorbed between about λ 2440 to λ 2329; the Cd lines 2329, 2321, 2313, and 2265 were well marked. Beyond this there was general absorption.

The rays were absorbed from the sharp line λ 2420 to Cd λ 2329, which was well marked, and the Cd lines to 2265 were well marked. Beyond this there was general absorption.

From here there was a complete, although weak, transmission of rays up to Cd 2329, the Cd lines to 2265 being well marked.

21 bands

176 mm.

λ .
2578 v.w., narr.
2549 " wide
2545 " narr.
2542 w., wide
{ 2539 " "
{ 2535 " "
{ 2530 " "
2528 " "
2525 " "
{ 2523 " "
{ 2521 " "
{ 2517 v.w., wide
{ 2512 " "
{ 2506 " "
{ 2500 " "
{ 2495 " "
{ 2489 " "

21 bands

22 bands

26 mm.

λ .
2577 v.w., narr.
2549 " wide
2545 " "
{ 2539 " "
{ 2534 " "
{ 2529 " "
2525 " "
2522 " "
{ 2517 " "
{ 2512 " "
{ 2506 " "
{ 2500 " "
{ 2495 " "
{ 2489 " "
{ 2461 " "
{ 2455 " "
{ 2449 " "

TABLE VIII (*continued*).

176 mm.		26 mm.	
λ .		λ .	
2461	v.w., wide	2442	v.w., wide
2455	" "	2438	" "
2449	" "	Complete transmission of the rays from here, the Cd lines being very strongly marked to λ 2194, but Cd 2144 was absent.	
2442	" "		
2438	" "		
From here the rays were completely transmitted, the Cd line 2194 was quite clear.			
22 bands		19 bands	

The table shows that, at the reduced pressures, there was a decrease in the total number of bands when compared with the observations of the vapour vibrating under increased pressures and temperatures. The decrease was more pronounced on the less refrangible side of the spectrum. The most persistent bands were the wide, well-marked bands, some of which have been arranged in groups of three. As the pressure decreased, the amount of vapour in the tube gradually diminished, and some of the weak bands disappeared, although the strong, wide bands were still easily seen. At the reduced pressures, the bands began to show their constituent members, as, for example, in 2118 and 2515, which appear to be two of the constituents of the band 2519 at increased pressures and temperatures.

TABLE IX.

The absorption bands of piperidine at a constant temperature of 100° and at different pressures. Barometric pressure = 762 mm.

Abbreviations: v.w. = very weak; narr. = narrow; w. = weak.

762 mm.		632 mm.		482 mm.	
λ .		λ .		λ .	
2579	v.w., wide	2579	v.w., narr.	2579	v.w., narr.
2589	" "	2542	" wide	2549	" "
2533	" "	2539	" "	2546	" "
2529	" "	2533	" "	2542	w., wide
2521	" "	2529	" "	2539	" "
2518	" "	2522	" "	2533	" "
2512	" "	2518	" "	2529	" "
2506	" "	2512	" "	2522	" "
2500	" "	2505	" "	2518	" "
General absorption from about λ 2450, the Cd 2470 being just visible.		2500	" "	2512	" "
		2495	" "	(2505)	" "
		2489	" "	2500	" "
		2484	" "	2495	" "
		2479	" "	2490	" "
General absorption from about Cd 2470, this line being sharp on the more refrangible edge.				2462	" "
				2456	" "
				2450	" "
				Absorption of rays from about λ 2450 to the Cd lines 2321 and 2313, which were visible.	

TABLE IX (*continued*).

The absorption bands of piperidine at* a constant temperature of 100° and at different pressures. Barometric pressure=762 mm.

Abbreviations: v.w.=very weak; narr.=narrow; w.=weak.

332 mm.			182 mm.			32 mm.		
λ .			λ .			λ .		
2578	v.w.,	narr.	2541	v.w.,	wide	2539	v.w.,	wide
2541	"	wide	2539	"	"	2533	"	"
{ 2539	"	"	{ 2533	"	"	{ 2529	"	"
{ 2532	"	"	{ 2529	"	"	{ 2460	"	"
{ 2529	"	"	{ 2522	"	"	{ 2455	"	"
{ 2522	"	"	{ 2518	"	"	{ 2449	"	"
{ 2518	"	"	{ 2513	"	"	Complete transmission of all rays to λ 2194.		
{ 2512	"	"	{ 2506	"	"			
{ 2505	"	"	{ 2500	"	"			
{ 2500	"	"	{ 2495	"	"			
{ 2495	"	"	{ 2490	"	"			
{ 2490	"	"	{ 2460	"	"			
{ 2462	"	"	{ 2455	"	"			
{ 2457	"	"	{ 2450	"	"			
{ 2451	"	"						

Almost complete transmission of rays to Cd 2329, although the rays between λ 234 and λ 232 were weak; the Cd lines 2321, 2313, and 2265 were clear.

Complete transmission of the rays to λ 2265.

15 bands

14 bands

6 bands

The table shows that at first there was an increase in the number of bands, which then decreased as the amount of vapour in the tube decreased. The most persistent bands were those which were wide and diffuse, and essentially characteristic of piperidine vapour.

General Results and Conclusions.

The chief results of these observations are that:

1. Pyridine vapour under varying conditions of temperature and pressure exhibits a considerable number of absorption bands, most of which can be arranged in groups in possessing somewhat similar appearances and in having regular differences in their wave-lengths. As the temperature and pressure increase, the positions of the bands do not appear to alter, but they become wider; weak bands become stronger, and new bands make their appearance; and the general absorption is shifted towards the less refrangible region. With decreased pressures the bands become sharper, many bands disappear, and the region of general absorption is shifted towards the more refrangible side of the spectrum. Besides these smaller

bands, there is a large band the position of which, relatively to the smaller ones, is on the more refrangible side of the spectrum.

2. α -Picoline vapour, under similar conditions of temperature and pressure, exhibits a number of bands which are similar to some of those of pyridine. The number of bands is, however, considerably less than in the vapour of pyridine, and the region of general absorption is shifted more towards the less refrangible rays. A few bands appear which are not observed in pyridine vapour. As the pressure is decreased, the same phenomena are observed as in pyridine vapour. The vapour of α -picoline also exhibits a strong absorption band in the ultra-violet region comparable with that observed in pyridine.

3. The vapours of the two lutidines and of trimethylpyridine, under similar conditions of temperature and pressure, do not exhibit any of the narrow bands characteristic of either pyridine or α -picoline; but they show the presence of a strong absorption band in the ultra-violet region analogous to the band found in pyridine and α -picoline. Besides that, the general absorption of the trimethylpyridine vapour is shifted more towards the red end of the spectrum when compared with the positions of general absorption of the two lutidines or of pyridine and α -picoline.

4. The vapour of piperidine exhibits a number of bands which can be differentiated into groups, and which are quite unlike those of pyridine; their positions are more towards the more refrangible rays. They are not altered in position by increasing the temperature and pressure, although they become wider and more diffuse, whilst the position of general absorption is shifted towards the red end of the spectrum. As in pyridine and α -picoline, the bands become sharper under decreased pressure, and the general absorption is rapidly shifted towards the more refrangible end of the spectrum.

In discussing the results, it is important to notice that Hartley (*loc. cit.*) has shown that the vapours of benzene and its homologues showed very similar phenomena. For example, the number of bands in the vapours of *o*-, *m*-, and *p*-xylenes, 1-methyl-4-propylbenzene, and 1:3:5-trimethylbenzene (mesitylene) were comparatively few when compared with the number of bands in benzene vapour. For example, in the case of mesitylene, only four weak bands are recorded, whilst benzene vapour gave a maximum number of 82 bands. It should also be mentioned that Hartley (*Trans.*, 1885, **47**, 685) in the case of pyridine and picoline, that Baker and Baly (*Trans.*, 1907, **91**, 1122) in the case of pyridine, α - and β -picolines, and 2:6-lutidine, and that Purvis and Foster (*Proc. Camb. Phil. Soc.*, 1907, **14**, 381) in the

case of 2:4:6-trimethylpyridine, have pointed out that the persistency of the absorption curves of the single absorption band, characteristic of these substances in alcohol, is gradually diminished with the increase in the number of methyl groups; so that, for example, the persistency of the absorption curve of trimethylpyridine is less than that of the lutidines, and of course much less than that of pyridine or the picolines. Besides these phenomena, the weighting of the molecule produces a shift of the band, and of the general absorption, towards the red end of the spectrum.

Now, very similar phenomena are observed in the spectra of the vapours of pyridine and its derivatives. The pyridine vapour exhibits a considerable number of narrow bands, most of which disappear in α -picoline, and all of which disappear in the lutidines and in trimethylpyridine. The disappearance of the bands, as the number of methyl groups in the pyridine ring increases, is analogous to the lessened persistency of the absorption band as the number of methyl groups is increased when the substances are examined in alcoholic solution. At the same time, a strong band in the ultra-violet remains throughout the vapours examined.

Hartley (Trans., 1885, **47**, 685) found no bands in alcoholic solutions of piperidine, and the author has confirmed this observation by examining $N/10$ - and $N/1000$ -solutions of piperidine in alcohol. But the vapour of the substance exhibits a considerable number of well-marked bands. The vibrations of the atoms in the molecules in the vaporous condition produce results which are completely different from those produced when the substance is dissolved in alcohol. Baker and Baly (*loc. cit.*) explained the absence of bands in solutions of piperidine from a consideration of the saturation of the valencies of the various atoms. But as has been already pointed out by the author (Trans., 1909, **95**, 294), the possibility of the presence of bands in the ultra-red regions of the spectrum cannot be ignored. In fact, Coblentz (*Astrophys. J.*, 1904, **20**, 207) in this region found one band in solutions of piperidine; and, in any case, the presence of so many bands in the vapour is opposed to an explanation from the valency saturation of piperidine. The effect on the production of bands by the addition of hydrogen atoms to the pyridine nucleus in piperidine vapour is different from the effects observed when one or more of the hydrogen atoms are replaced by methyl groups.

The general absorption is considered to be produced by the movements of the molecules themselves, whilst the selective absorption is produced by the movements of the atoms of the molecules. These vibrations are influenced by various conditions, such as the nature, weight, type, and orientation of the constituent atoms. In

addition to these regulating influences, the extent of the free path of the vibrating molecules should be considered, and the forces which will influence this will be whether the substance is in solution or in the vaporous state, and how far the vibrations are modified by the energy of the light waves which pass through the one or the other. If these encounters are modified in any of the suggested ways, such as the number and type and orientation of the atoms of the nucleus, the oscillations or vibrations will also be modified, and the absorption spectra will be different. In the case of pyridine, the accepted chemical formula indicates a symmetrical relationship of the atoms, whilst in the case of the methyl derivatives of the substance, the symmetry is destroyed. It is conceivable, therefore, that an unsymmetrical orientation of the atoms may imply a dislocation in the oscillations or vibrations of the atoms. Or, to express it another way, the methyl group in α -picoline may not only influence the fundamental vibrations of the atoms of the ring, but it may act as a kind of buffer which absorbs a part of the energy of the encounters. The decreased influence on the vibrations of α -picoline is exhibited in a decrease in the number of bands of selective absorption characteristic of pyridine. Now, in the two lutidines and in trimethylpyridine, the protective influence of the two and three methyl groups respectively lessens the amount of energy absorbed by the encounters between the molecules to such an extent as not to influence the oscillations or vibrations of the atoms, and the bands completely disappear. One strong band remains which is characteristic of these substances both in alcoholic solutions and in the vaporous condition, although, of course, their positions are different; and it may be considered to be the result of the rhythmical vibration or oscillation or pulsation of the nucleus as a whole.

The encounters of the molecules when in solution in alcohol will be considerably altered, and the energy will be partly absorbed by the solvent itself, so that the vibrations of the atoms cannot be influenced in the same way as when the molecules are in the vaporous state. The fundamental vibration or pulsation of the ring will remain, and this is made evident by the single band of pyridine and its lessened persistency in α -picoline, the lutidines, and trimethylpyridine.

As the temperature and pressure rise, the movements of the molecules will become more rapid, with the result that the number of molecules passing the radiant energy of the source of light in a given time will increase, as will also the amount of absorption. The number of encounters will also increase, and the

more frequent and rapid bombardments will produce a greater dislocation or oscillation or vibration of the constituent atoms, the resultant influence of which is seen in the production of widened absorption bands. When the pressure is decreased, the number of encounters in a given time will decrease, and there will be a decrease in the number of bands, and the others will become sharper, whilst the region of general absorption will be shifted towards the more refrangible end of the spectrum.

The argument receives support from the phenomena observed in piperidine vapour. The accepted constitutional formula for the substance implies a regular and symmetrical orientation of the atoms; and it is a fair corollary that the vibrations of the atoms will be regular and symmetrical. The vapour of piperidine exhibits a considerable number of bands, although a less number than in the vapour of pyridine, most of which are wide and characteristic. On the above explanation, the bands owe their origin to the transference to the atoms of a part of the energy of the encounters of the molecules. As the added hydrogen atoms have less mass than any of the methyl groups, and as they do not distort the implied symmetry of the molecule, as in the replacement of hydrogen by methyl groups, they do not completely protect the atoms of the nucleus from the influence of the encounters. The result is apparent in a diminished number, and a difference in position and in character of the bands of piperidine as compared with those of pyridine. The vibrations of the atoms of the nucleus are influenced by the addition of the hydrogen atoms, so that the resultant effect is a change in the number, character, and position of the bands. There is no obliteration of bands as in α -picoline, the two lutidines, and trimethylpyridine; and, also, as in pyridine and its methyl derivatives, the bands are widened with increased temperature and pressure.

I desire to convey my thanks to the Government Grant Committee of the Royal Society, by whose grant the larger portion of the cost of the apparatus used in this research was defrayed; and also to Dr. Sell, who was good enough to give me the pure pyridine, the α -picoline, and the 2:4:6-trimethylpyridine.

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XLVII.—*The Addition of Bromine to Unsaturated Compounds. Part I.*

By JOHN JOSEPH SUDBOROUGH and JOHN THOMAS.

IN a preliminary note (Proc., 1906, **22**, 318) we were able to show that the reaction between cinnamic or crotonic acid and bromine in carbon tetrachloride solution is a typical bimolecular reaction, and that the replacement of the acid by a methyl or ethyl ester affects the velocity of addition only to a very slight extent. It was also pointed out that the reaction is influenced to an appreciable extent by light, the effect of bright sunlight raising the constant some 200 times its value in the dark.

Subsequent experiments have proved that the addition of bromine to $\alpha\beta$ -unsaturated acids takes place but slowly, whereas isomeric $\beta\gamma$ -acids, or, generally, olefine acids in which the double linking is not in the $\alpha\beta$ -position with regard to the carboxyl group, unite with bromine extremely readily, and we have suggested (Proc., 1907, **23**, 147) this as a method of determining in any given acid whether the double linking is in the $\alpha\beta$ -position or not.

Hugo and Bauer (*Ber.*, 1904, **37**, 3317) have drawn attention to the inhibiting effect on the addition of bromine which the presence of several negative radicles, such as CO_2H , CO_2R , Ph, Br, and CN, in the ethylene molecule produces; but they have not determined the velocities of the reactions in any case.

Herz and Mylius (*Ber.*, 1906, **39**, 3817) have conducted experiments on the addition of bromine to cinnamic acid in chloroform solution. They worked with sealed bulbs placed in a thermostat, and at the end of the given time broke the bulbs under potassium iodide solution. They found that the reaction was bimolecular, and that certain impurities, especially iodine, had a considerable accelerating action. The combination was also found to be somewhat quicker in carbon tetrachloride than in chloroform solution, and still quicker in carbon disulphide solution; but in the latter case the values for K varied considerably.

Still more recently K. A. Hofmann and Kirmreuther (*Ber.*, 1909, **42**, 4481) have examined the addition of bromine to the chloroethylenes. They used a large excess of the chloroethylene, and found that the reaction became practically unimolecular. The results prove that dichloroethylene combines with bromine more readily than tetrachloroethylene. With trichloroethylene the values obtained for K varied considerably, and with both tri- and tetra-chloro-derivatives the reaction was disturbed by the production of a catalyst, probably carbonyl chloride.

Barrett and Lapworth (Proc., 1907, **23**, 18) have studied the addition of bromine to certain unsaturated acids in aqueous solution. With cinnamic acid, even in 0.001*N*-solutions, the reaction proceeds so quickly that the time has to be measured in seconds, and it was found that nearly the whole of the bromine was combined in thirty seconds. With crotonic acid the addition was not quite so rapid. The sodium salts were also used, and the effect of introducing potassium bromide into the mixture was examined.

Bauer and Moser (*Ber.*, 1907, **40**, 918) have studied the addition of bromine to stilbene and to methylstilbene in chloroform, and also in carbon tetrachloride solution. They found that the presence of the methyl group facilitates the addition of the halogen, and also proved that the reaction between bromine and α -phenylcinnamionitrile is a balanced one.

In all our experiments we have used carbon tetrachloride as solvent. We selected this solvent as the molecule does not contain hydrogen atoms which can react with the halogen. The solvent was purified by shaking with dilute alkali, then with dilute hydrochloric acid, and finally with water until free from acid. It was then kept for a day over fused calcium chloride and distilled over phosphoric oxide. We conducted experiments in order to determine whether the cinnamic acid or its additive compound, $\alpha\beta$ -dibromo- β -phenylpropionic acid, had any action on sodium thiosulphate. This was necessary, as in all our experiments the concentration of the unaltered bromine, and hence of the cinnamic acid, was determined by the addition of potassium iodide solution and the titration of the free iodine by means of standard thiosulphate solution. Twenty c.c. of a 0.05*N*-solution of thiosulphate required 18.95 c.c. of standard iodine solution; 20 c.c. of the same solution were shaken for some minutes with 20 c.c. of a 0.066*N*-solution of cinnamic acid in carbon tetrachloride. In three experiments the amounts of iodine were 18.95, 18.90, and 18.95 c.c. respectively. Similar experiments were conducted with a 0.066*N*-solution of $\alpha\beta$ -dibromo- β -phenylpropionic acid; 20 c.c. of thiosulphate required 18.95 c.c. of iodine, and three mixtures of thiosulphate and dibromide required respectively 19.05, 19.10, and 19.10 c.c. of iodine. These results indicate that there is a slight reaction between the bromo-acid and the thiosulphate, but we are of the opinion that even this effect will not be met with in the actual titrations, as an excess of thiosulphate is never present during the titration, and the amount of dibromo-acid is always considerably less than the amount used in the above experiments.

In the determination of the amount of uncombined bromine by

adding potassium iodide and titrating the liberated iodine by means of standard thiosulphate and starch, it was noticed that after the titration was completed the blue colour was restored in the course of a short time. This appears to be due to the fact that the cinnamic acid dibromide can slowly liberate iodine from potassium iodide. A solution of cinnamic acid dibromide in carbon tetrachloride when kept for a week did not give a blue coloration with potassium iodide and starch, indicating that the dibromo-acid does not give rise to free bromine, but when the above mixture was kept for half an hour a distinct blue colour was observable. It is thus necessary to titrate the liberated iodine immediately after the addition of the potassium iodide.

The following numbers obtained with carbon tetrachloride solutions of cinnamic acid and bromine at 15° in colourless glass bottles in diffused daylight indicate that the reaction is bimolecular :

$C_{\text{acid}} = 52.72.$		$C_{\text{Br}} = 26.25.$
t (in hours).	$a - x.$	$K = \frac{1}{(a-b)t} \log \frac{b(a-x)}{a(b-x)}.$
0.25	20.65	1.92×10^{-2}
0.50	15.05	1.66
0.75	12.60	2.19
1.00	12.50	1.66
1.25	9.30	1.96
1.50	8.10	1.90

The effect of light was clearly shown by two sets of experiments with ethyl cinnamate and bromine at 15° ; the one series was carried out in colourless bottles in fairly bright sunlight, and the other in amber-coloured bottles in the dark. The value for K obtained in the first set was 4.0×10^{-2} , and $7/8$ ths of the bromine were used up at the end of an hour and a-half. In the second series of experiments only $1/24$ th of the bromine had been used up in the same time (1.5 hours).

Comparative experiments with crotonic acid in the dark and in ordinary daylight were also made. The solutions of acid and of bromine were of equivalent strength (practically $1/30$ th of the gram-molecule per litre). The constant calculated from the formula $K = 1/t.x/a(a-x)$ varied between 1.7×10^{-5} and 2.4×10^{-5} in the dark, and between 2.6×10^{-3} and 4.9×10^{-3} in daylight. Somewhat similar results were obtained with cinnamic acid and methyl cinnamate.

In all the above-mentioned experiments the bromine was purified by shaking with concentrated sulphuric acid. In subsequent experiments the bromine used was subjected to the following method of purification. About 150 c.c. were shaken with concentrated sulphuric acid, and the clear liquid was run into a test-tube surrounded by a freezing mixture of calcium chloride and ice.

After the bromine had solidified, the tube was removed from the freezing mixture, and the portion which melted first was poured off. This process was repeated several times, until about 50 grams were obtained, melting at -6° to -7° .

The general method of procedure was to make carbon tetrachloride solutions of the unsaturated compound and of bromine of the same concentration (namely, 250 c.c. of a solution containing 1/30th of the gram-molecular weight per litre). The two solutions were standardised, the acid solution by means of standard barium hydroxide solution, using phenolphthalein as indicator, and the bromine solution by means of potassium iodide and thiosulphate, using starch as indicator. When esters were used, the ester solution was not standardised, but was made of the strength required by weighing out the exact amount necessary. The two solutions were placed in the thermostat regulated for 15° , and after some little time equal volumes of the two were mixed in the dark. Thirty c.c. of the mixture were run into each of several brown bottles, and these were kept in the dark at 15° . At the end of the given time excess of potassium iodide solution was added, the whole removed to a colourless bottle, and titrated with standard thiosulphate. Several litres of the thiosulphate were prepared and stored in a large bottle attached to the burette. The thiosulphate was protected from atmospheric carbon dioxide by means of a soda-lime tower. As the two solutions were of equivalent strength, the equation $K = 1/t \cdot x/a(a-x)$ was used for calculating K . The values for a and $a-x$ were denoted by the number of c.c.'s of thiosulphate required at the beginning and after given intervals of time. As the same number of c.c.'s of mixture were used in each case, and as the thiosulphate solution was the same throughout, the values for K given in the following table are comparable. In this table $a = 25.30$ c.c. (of thiosulphate). In all cases t in the equation $K = 1/t \cdot x/a(a-x)$ is calculated in hours.

The compounds used in these experiments were all purified before use. The values of K obtained for any given compound are not very concordant. Other authorities have noticed this fact (compare Herz and Mylius; Hofmann and Kirmreuther, *loc. cit.*). The only reason for this that we can offer is that a trace of some impurity has a considerable effect on the velocity of the reaction.

When acids were used in which the double linking was not in the $\alpha\beta$ -position, the reaction proceeded so rapidly that titrations every few seconds were necessary. Under such conditions the experimental errors which arise in measuring t are great, and a close agreement between the values of K is not to be expected.

The conclusions we draw from these experiments are: (1) The

TABLE I.

Unsaturated compound.	Formula.	Series.	Maximum time.	Number of titrations.	1/t. $w/a(a-w)$.	
					Minimum.	Maximum.
Crotonic acid :						
	CHMe:CH·CO ₂ H	a	332 hours	4	1·8 × 10 ⁻⁵	2·4 × 10 ⁻⁵
Cinnamic acid :						
	CHPh:CH·CO ₂ H	a	240 „	4	1·8 × 10 ⁻⁴	2·6 × 10 ⁻⁴
		b	120 „	5	0·9 × 10 ⁻⁴	1·4 × 10 ⁻⁴
Methyl cinnamate :						
	CHPh:CH·CO ₂ Me	a	143 „	5	1·22 × 10 ⁻⁴	2·35 × 10 ⁻⁴
		b	146 „	3	1·41 × 10 ⁻⁴	2·21 × 10 ⁻⁴
Ethyl cinnamate :						
	CHPh:CH·CO ₂ Et	a	122 „	5	1·2 × 10 ⁻⁴	1·7 × 10 ⁻⁴
		b	240 „	5	1·1 × 10 ⁻⁴	1·3 × 10 ⁻⁴
		c	144 „	5	1·3 × 10 ⁻⁴	2·6 × 10 ⁻⁴
β-Ethylacrylic acid :						
	CHEt:CH·CO ₂ H	a	265 „	4	3·3 × 10 ⁻⁵	6·0 × 10 ⁻⁵
αβ-Oleic acid :						
	CH ₃ ·[CH ₂] ₁₄ ·CH:CH·CO ₂ H	a	173 „	4	2·3 × 10 ⁻⁵	2·6 × 10 ⁻⁵
Phenyl-βγ-crotonic acid :						
	CHPh:CH·CH ₂ ·CO ₂ H	a	120 secs.	4	3·5	6·3
		b	120 „	4	2·6	4·8
Allylacetic acid :						
	CH ₂ :CH·CH ₂ ·CH ₂ ·CO ₂ H	a	30 „	4	1·4 × 10 ²	2·3 × 10 ²
		b	30 „	4	1·4 × 10 ²	2·2 × 10 ²
Ethylidenepropionic acid :						
	CH ₃ ·CH:CH·CH ₂ ·CO ₂ H	a	60 „	4	10·0	48·0
		b	60 „	4	11·0	58·0
Undecylenic acid :						
	CH ₂ :CH·[CH ₂] ₈ ·CO ₂ H	a	480 „	5	0·5	1·4
		b	480 „	4	0·7	1·5
Oleic acid :						
	CH ₃ ·[CH ₂] ₇ ·CH:CH[CH ₂] ₇ ·CO ₂ H	a	60 „	4	14·0	31·3
		b	75 „	5	12·7	30·9
Elaidic acid :						
	CH ₃ ·[CH ₂] ₇ ·CH:CH[CH ₂] ₇ ·CO ₂ H	a	120 „	5	2·9	10·7
		b	120 „	5	3·0	11·8
Erucic acid :						
	CH ₃ ·[CH ₂] ₇ ·CH:CH[CH ₂] ₁₁ ·CO ₂ H	a	120 „	4	3·0	15·7
		b	120 „	4	3·1	14·6
Brassicidic acid :						
	CH ₃ ·[CH ₂] ₇ ·CH:CH[CH ₂] ₁₁ ·CO ₂ H	a	90 „	4	3·5	7·4
		b	120 „	4	3·1	7·1

reaction between bromine and an olefine acid in carbon tetrachloride solution is bimolecular, and is practically non-reversible. (2) The rate of addition is accelerated to an enormous extent under the influence of light. (3) The reaction is comparatively slow with all αβ-unsaturated acids, but is completed in the course of a few minutes, when the double linking is further removed from the carboxylic group. According to Hugo and Bauer (*loc. cit.*), this is to be attributed to the "negative" character of the carboxylic group rather than to any stereochemical effects.

The difference between the rate of esterification of an αβ-unsaturated and its βγ- or γδ-isomeride (*Trans.*, 1907, **91**, 1033;

1909, **95**, 315) and the difference in the rates of addition of bromine afford two simple methods for determining whether the double linking in a simple olefine acid is in the $\alpha\beta$ -position or not.

In conclusion, we desire to thank the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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XLVIII.—*Studies in the Diphenyl Series. Part I.* *Acetylation of Benzidine Derivatives.*

By JOHN CANNELL CAIN and PERCY MAY.

In a previous communication (Trans., 1909, **95**, 714) it was shown by one of us that when aqueous-alcoholic solutions of benzidine or tolidine are treated with a molecular proportion of acetic anhydride in the cold (compare Pinnow, *Ber.*, 1900, **33**, 417), a large proportion of the base is converted into the monoacetyl derivative, the proportion of monoacetyl to diacetyl compound being roughly two to one in the case of benzidine and three to one in the case of tolidine. It was also mentioned that dianisidine, under the same conditions, furnishes no diacetyl compound.

It was thought, therefore, that it would be of interest to study this reaction further, with the view of throwing some light on the influence of substituents in the acetylation of benzidine derivatives, and this has been done by acetylating various bases of the diphenyl series in the above manner, and determining the relative amounts of mono- and di-acetyl derivatives formed. The results of these experiments are given in the following table:

Base.	Proportion in product of:	
	Monoacetyl.	Diacetyl.
Benzidine	65 per cent.	35 per cent.
3 : 3'-Dimethylbenzidine (tolidine)	75 ,,	25 ,,
3 : 3'-Dimethoxybenzidine (dianisidine).	only product	—
3 : 3'-Dichlorobenzidine	chief ,,	small amount
2 : 2'-Dichlorobenzidine	75 per cent.	25 per cent.
2 : 2'-Dinitrobenzidine	trace	none
2-Nitrobenzidine	only product	—
3-Ethoxybenzidine	75 per cent.	25 per cent.

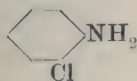
In those cases where no diacetyl compound was formed by this method, it was prepared for purposes of comparison by boiling the dry substance with acetic anhydride.

From the above table it will be seen that the reactivity of the amino-groups in the benzidine molecule is considerably diminished by the introduction of substituents. Considering first those disubstituted derivatives in which each substituent is in the ortho-position with respect to the amino-group, it will be noticed that the introduction of the methyl group (tolidine) produces the least effect; the diminution in the amount of diacetyl derivative can only, we think, be attributed to steric hindrance. When, however, the substituent groups are negative, the effect is very much greater, a very small amount of diacetyl compound being produced in the case of the dichloro-derivative, none in the case of the dimethoxy-derivative, and in the case of the dinitro-derivative the inhibition is so great that only a very small amount of the monoacetyl compound is obtained. Moreover, the fact that 2:2'-dichlorobenzidine (where the chlorine atoms are in the meta-position with respect to the amino-groups) furnishes about 25 per cent. of the diacetyl compound points to the conclusion that in the case of negative substituents in the ortho-position with respect to the amino-groups, steric hindrance also plays a part in inhibiting the acetylation.

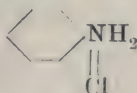
What, however, is the cause of the increased effect of the negative groups in this reaction? That negative groups have the same effect in the acetylation of amines of the benzene series has also been shown by Ulfers and von Janson (*Ber.*, 1894, **27**, 93), who performed their experiments under widely different conditions at high temperatures.

The question raises the much greater one of the general effect of the introduction of negative substituents on groups or atoms already in the molecule. We have no intention of enlarging on this point, but attention may be directed to the fact that in modern chemical constitutional formulæ there is nothing to indicate any relationship between groups which undoubtedly influence each other, a relationship which undoubtedly exists.

We are inclined to suggest that when a negative atom or group is introduced into a base, thus, for example, in the case of *o*-chloroaniline (and, in a less degree, perhaps the *m*- and *p*-derivatives), it is possible that the constitution is not truly represented by the formula (I), but that the residual affinities of the nitrogen and chlorine atoms come into play, with the result



(I.)



(II.)

that the compound is more correctly represented by the formula

(II). A similar configuration would be assigned to those bases containing an oxygenated substituent, the oxygen thereby becoming quadrivalent. The effect of this in acetylation would be that the amino-group, being thus bound or influenced by the negative substituent, would be more difficult of attack than when free, as in aniline. We put this suggestion forward tentatively, but it is significant that Ulfers and von Janson (*loc. cit.*) found that when the acetyl group had been introduced into a negatively ortho-substituted monoamine, the same substituent facilitated (no longer retarded?) the introduction of a second acetyl group to form a diacetyl compound. The explanation may be that after the breaking of the double linking between chlorine and nitrogen, the basicity of the acetylated amino-group is so weak that a union with chlorine can no longer take place.

The effect of introducing one substituent in the benzidine molecule is what was to be expected from what has been shown to take place in the case of the disubstituted derivatives. The 2-nitro-derivative furnishes no diacetyl, but a quantitative yield of the monoacetyl compound, whilst the 3-ethoxy-derivative gives rise to both compounds, but the amount of diacetyl derivative is less than that produced in the case of benzidine itself.

For the purpose of comparison, aniline and *m*-nitroaniline were acetylated in the same way. In the former case a nearly quantitative yield of acetanilide was obtained, but in the latter most of the base was recovered unchanged, only about 10 per cent. of *m*-nitroacetanilide being produced.

EXPERIMENTAL.

The preparation of monoacetyl-benzidine and -tolidine has already been described (Cain, *loc. cit.*). It has since been found that Biehringer and Borsum (*Ber.*, 1906, **39**, 3348) described a monoacetyl-*o*-tolidine as being produced by heating the base with the diacetyl derivative. This compound is stated to form pale yellow crystals, melting at 133–135°, becoming green when exposed to the atmosphere, and decomposing when moist at 100°. The product obtained by one of us crystallises in white, shining plates, containing one molecule of water of crystallisation, and melting at 103°. Its constitution was fully proved, and it can only be concluded that Biehringer and Borsum's compound had not the constitution assigned to it, especially as it was stated to crystallise from water, apparently in the anhydrous state.

Acetylation of Dianisidine.

The acetylation of this and the other bases described in this paper was carried out as previously mentioned (*loc. cit.*, p. 717).

Monoacetyldianisidine,* $\text{NHAc} \cdot \text{C}_{14}\text{H}_{12}\text{O}_2 \cdot \text{NH}_2 \cdot \text{H}_2\text{O}$, is readily soluble in alcohol, and crystallises from water in white nodules, melting at 67° . The water of crystallisation is lost at 100° , and the anhydrous substance melts at 116° :

0.1448 gave 11.8 c.c. N_2 at 20° and 758 mm. $\text{N} = 9.5$.

$\text{C}_{16}\text{H}_{18}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$ requires $\text{N} = 9.2$ per cent.

Acetylation of 3: 3'-Dichlorobenzidine.

3: 3'-*Dichloroacetylbenzidine*,* $\text{NHAc} \cdot \text{C}_{12}\text{H}_6\text{Cl}_2 \cdot \text{NH}_2$, dissolves readily in alcohol, but sparingly in water, and forms white, feathery needles, melting at $104\text{--}105^\circ$:

0.0837 gave 6.8 c.c. N_2 at 19° and 756 mm. $\text{N} = 9.5$.

$\text{C}_{14}\text{H}_{12}\text{ON}_2\text{Cl}_2$ requires $\text{N} = 9.5$ per cent.

3: 3'-Dichlorodiacetylbenzidine has been mentioned incidentally in Eng. Pat. 25725 of 1896 (I. Levinstein and Levinstein, Ltd.). It crystallises from glacial acetic acid in slender, white needles, melting at 302° .

Acetylation of 2: 2'-Dichlorobenzidine.

This base was first obtained by Laubenheimer (*Ber.*, 1875, 8, 1625) from *m*-chloronitrobenzene by conversion first into dichloro-azoxybenzene and then into the hydrazo-compound. We have prepared the latter direct by reducing *m*-chloronitrobenzene in the modern manner with zinc and sodium hydroxide, and subsequently effecting the "benzidine change" by means of hydrochloric acid. The base crystallises from water in white needles, melting at 165° (Laubenheimer obtained small, flat prisms from alcohol, *m. p.* 163°).

In the acetylation no insoluble diacetyl compound separated from the hot solution, but, on dilution and cooling, the crystals which were obtained were found to consist of a mixture of the mono- with the di-acetyl compound, and were separated by means of dilute hydrochloric acid. The diacetyl compound is soluble in 50 per cent. aqueous alcohol, and thus differs from most of the other diacetyl compounds of this class.

2: 2'-*Dichloroacetylbenzidine*, $\text{NHAc} \cdot \text{C}_{12}\text{H}_6\text{Cl}_2 \cdot \text{NH}_2$, separates

* This compound was described at the International Congress of Applied Chemistry, London, 1909. The diacetyl compound (*m. p.* 231°) was prepared by Starke (*J. pr. Chem.*, 1899, [ii], 59, 214).

from hot water in white, feathery crystals, melting at 195° . It is readily soluble in glacial acetic acid or alcohol, sparingly so in ether, chloroform, or ethyl acetate, and insoluble in benzene:

0.1765 gave 15.0 c.c. N_2 at 18° and 759 mm. $N=10.0$.

$C_{14}H_{12}ON_2Cl_2$ requires $N=9.5$ per cent.

2: 2'-*Dichlorodiacetylbenzidine*, $NHAc \cdot C_{12}H_6Cl_2 \cdot NHAc$, crystallises from glacial acetic acid, in which it is very soluble, in short, white needles, melting above 310° . It is moderately soluble in alcohol, and insoluble in hot water, ether, acetone, ethyl acetate, or chloroform:

0.1098 gave 8.0 c.c. N_2 at 17° and 761 mm. $N=8.6$.

$C_{16}H_{14}O_2N_2Cl_2$ requires $N=8.3$ per cent.

Acetylation of 2: 2'-Dinitrobenzidine.

The base was prepared by nitrating benzidine as described by Täuber (*Ber.*, 1890, **23**, 795), and was found to possess all the characteristics attributed to it by him. From the mother liquors, however, after crystallising the product of nitration, beautiful yellow needles were obtained, which melted at 198° (Täuber's dinitrobenzidine, like ours, crystallised in leaflets, melting at 214°). These proved, on analysis, to be an isomeric dinitrobenzidine:

0.0917 gave 15.8 c.c. N_2 at 18° and 752 mm. $N=20.1$.

$C_{12}H_{10}O_4N_4$ requires $N=20.4$ per cent.

This compound seems to be identical with the dinitrobenzidine described by Bandrowski (*Monatsh.*, 1887, **8**, 472), which he obtained by the hydrolysis of dinitrodiphtalylbenzidine. Its melting point is given as $196-197^{\circ}$, and its constitution was not determined.

On acetylating 2: 2'-dinitrobenzidine under the stated conditions, only a minute trace of a monoacetyl derivative was formed, almost the whole of the base being recovered unchanged.

2: 2'-*Dinitrodiaacetylbenzidine* was, however, prepared by heating the base with acetic anhydride. It is insoluble in acetone, ether, or cold alcohol, sparingly soluble in hot alcohol or chloroform, and fairly so in glacial acetic acid, from which it separates in small, almost colourless needles, melting and decomposing above 290° :

0.1222 gave 15.5 c.c. N_2 at 15° and 770 mm. $N=15.3$.

$C_{16}H_{14}O_6N_4$ requires $N=15.6$ per cent.

Acetylation of 2-Nitrobenzidine.

The base was obtained from the technical product (sulphate), after recrystallisation from water, by neutralising with ammonia; it crystallised from water in dark red needles, melting at 143° .

2-Nitro-4'-acetylbenzidine, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_3(\text{NO}_2) \cdot \text{NH}_2$, was obtained in a quantitative yield by the acetylation of the base. The fact that 2: 2'-dinitrobenzidine does not yield any (or only a trace of) monoacetyl derivative under the same conditions would appear to be conclusive evidence in favour of the above constitution. The compound is soluble in alcohol, hot water, ethyl acetate, or glacial acetic acid, very sparingly so in ether, chloroform, or benzene, and insoluble in cold water. It crystallises from alcohol or hot water in yellow plates, melting at $186-187^\circ$:

0.1515 gave 20.3 c.c. N_2 at 21° and 764 mm. $\text{N}=15.7$.

$\text{C}_{14}\text{H}_{13}\text{O}_3\text{N}_3$ requires $\text{N}=15.5$ per cent.

2-Nitrodiacetylbenzidine, prepared by boiling the monoacetyl compound with acetic anhydride, is insoluble in water, alcohol, ethyl acetate, chloroform, ether, or benzene, but sparingly soluble in glacial acetic acid, from which it separates in small, white crystals, melting above 310° :

0.3212 gave 36.4 c.c. N_2 at 15° and 773 mm. $\text{N}=13.7$.

$\text{C}_{16}\text{H}_{15}\text{O}_4\text{N}_3$ requires $\text{N}=13.4$ per cent.

Acetylation of 3-Ethoxybenzidine.

The base was obtained by recrystallising the technical product from hot water. On acetylation it was found that, as in the case of 2: 2'-dichlorobenzidine, the diacetyl derivative was soluble in 50 per cent. aqueous alcohol, so that, on cooling the solution, a mixture of mono- and di-acetyl derivatives was obtained. This was separated by means of cold dilute hydrochloric acid.

4'-Acetyl-3-ethoxybenzidine, $\text{NHAc} \cdot \text{C}_{12}\text{H}_7(\text{OEt}) \cdot \text{NH}_2$ (the inhibitive effect of the ethoxy-group, as shown in the table on p. 720, renders it certain that the acetyl and ethoxy-groups are in different rings) dissolves in alcohol or hot water, but is insoluble in ether, benzene, or light petroleum. It crystallises from hot water in small, white leaflets, melting at $137-138^\circ$:

0.1029 gave 9.1 c.c. N_2 at 15° and 765 mm. $\text{N}=10.6$.

$\text{C}_{16}\text{H}_{18}\text{O}_2\text{N}_2$ requires $\text{N}=10.4$ per cent.

Diacetyl-3-ethoxybenzidine is readily soluble in glacial acetic acid or alcohol, sparingly so in ethyl acetate or chloroform, and insoluble in benzene or water. It crystallises from acetic acid or alcohol in small, white needles, melting at 240° :

0.1227 gave 9.25 c.c. N_2 at 15° and 755 mm. $\text{N}=9.2$.

$\text{C}_{18}\text{H}_{20}\text{O}_3\text{N}_2$ requires $\text{N}=9.0$ per cent.

We wish to express our thanks to Mr. A. S. Clark, B.Sc., for

assistance in preparing 2: 2'-dichlorobenzidine; to Messrs. Kalle and Co., for supplying us with a quantity of nitrobenzidine sulphate; and to the Research Fund Committee of the Chemical Society, for a grant towards the expenses of this investigation.

UNIVERSITY COLLEGE,
LONDON.

XLIX.—*The Change of Cobaltous into Cobaltic Nitrite.*

By TSUNEO SUZUKI.

VERY little is known of what happens to cobaltous nitrite when it is produced in solution in the absence of acids or dissolved salts. In 1860 the Swedish chemist, Lang, published the fact that such a solution of cobaltous nitrite left, on evaporation, blackish-brown crystals of highly basic cobaltic nitrite (*K. S. Vet. Akad. Handl.*, 1860; *Pogg. Ann.*, 1863, **118**, 282). According to Hampe (*Annalen*, 1863, **125**, 343), the red saline mass thus obtained contains cobaltous as well as cobaltic nitrite. Neither Lang nor Hampe gave quantitative results.

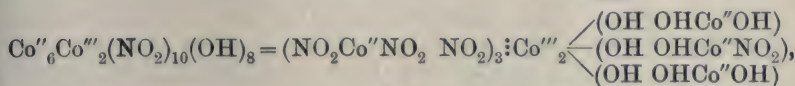
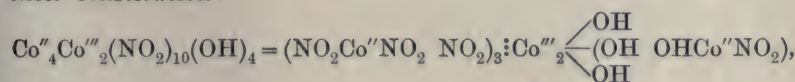
In order to obtain Lang's crystals, precipitated calcium carbonate suspended in a very little water was dissolved by passing in nitrous gases, cobaltous sulphate in equivalent quantity was added, and the calcium sulphate filtered off. Lang and Hampe both used barium nitrite, but the difficulty of separating barium sulphate, when precipitated from a cold neutral solution, made the use of calcium nitrite preferable in the present research. The filtrate from the calcium sulphate was evaporated almost to dryness in a vacuum desiccator at a temperature of 30°, and the residue treated with a little water, filtered from some calcium sulphate, and the solution left in the desiccator again to crystallise. The salt is too changeable to be safely recrystallised. It forms small, very dark red crystals, very soluble in water, and remarkable for being alkaline to litmus.

To analyse the salt, the cobalt was precipitated as cobaltous ammonium phosphate and weighed as cobaltous pyrophosphate (Dirvell and Clarke's process, as given in Dittmar's *Quantitative Analysis*, p. 309). The little cobalt left in solution was obtained by adding a drop of ammonium sulphide, and heating the cobalt sulphide so as to convert it into the black oxide, Co_3O_4 . The cobaltic cobalt in the salt was separately determined by digesting the salt with a concentrated warm solution of sodium carbonate and treating the residue twice with fresh sodium carbonate, the last time bringing the whole to boiling. The washed residue was

dissolved in dilute hydrochloric acid, holding potassium iodide in solution, and the cobalticum estimated iodometrically. The nitrite of the salt, which had been converted by the sodium carbonate into sodium nitrite, was estimated by the permanganate method.

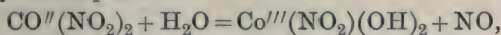
The results of analysis are expressed by the formula $\text{Co}''_{14}\text{Co}'''_6(\text{NO}_2)_{30}(\text{OH})_{16}, 34\text{H}_2\text{O}$, in which $\text{Co} : \text{N} = 2 : 3$, and the ratio of the valencies of the cobalt to those of the nitrogen atoms is as slightly more than $3 : 2$. The tabulated percentage numbers are: total cobalt,* f. 34.13, c. 34.26; cobaltic cobalt, f. 10.42, c. 10.28; nitrogen, f. 12.31, c. 12.21.

The formula calculated for the salt is resolvable into $2\text{Co}''_4\text{Co}'''_2(\text{NO}_2)_{10}(\text{OH})_4 + \text{Co}''_6\text{Co}'''_2(\text{NO}_2)_{10}(\text{OH})_8 + 34\text{H}_2\text{O}$, and in other similar ways. From what is known of cobaltic and other allied compounds, these constituent salts may have their formulæ expanded into the following, as probably accurate expressions of their constitution:

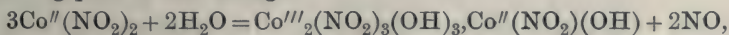


It is unnecessary to add to these formulæ the complex one for the crystalline salt as compounded of them. The apposition in them of NO_2 with NO_2 and of OH with OH serves to express, without pretending to explain, the pairing of acidic components so characteristic of such double salts as nitrites and cyanides. The NO_2 and OH groups next on either side to the Co'''_2 group represent, together with it, hemihydroxycobaltic nitrite, $(\text{NO}_2)_3\text{Co}'''(\text{OH})_3$, existent, probably, only in combination as a double nitrite. Cobaltous nitrite and hydroxynitrite are similarly displayed in these formulæ.

The self-conversion of cobaltous nitrite into cobaltic nitrite would be shown by the equation,



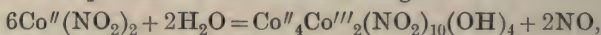
did all the cobalt nitrite ever become cobaltic, instead of but little more than one-third of it. As, however, the whole of the cobalt nitrite undoubtedly takes part in the change, this fact must be presented in the equation framed to express the conversion. This equation will be more readily followed by prefacing it with another, showing part of the change:



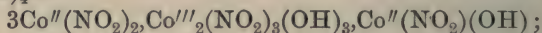
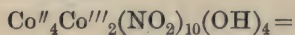
from which it will be seen that two cobalt atoms, in becoming cobaltic, pair together and lose only one nitroxyl group, the third

* The letters "f" and "c" stand for "found" and "calculated."

cobalt atom remaining cobaltous, although also losing a nitroxyl group. The equation of the actual change is



in which



that is, six molecules of cobalt nitrite become united, half of them unaltered, and the other three, with loss of 2NO and acquisition of 2H₂O, as cobaltic and cobaltous hemihydroxynitrites. This condensation of the six molecules into a complex happens without any union taking place of the atoms of cobalt with each other through the agency of their ordinary valencies, which are, it will be seen, used up in the union of the cobalt with the nitroxyl and hydroxyl atoms.

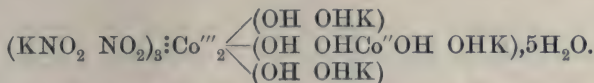
The change just formulated must be treated as indivisible, but other changes occur which may be regarded as secondary to it. There is evidently a cumulative resolution of the molecules of the $\text{Co}''_4\text{Co}'''_2(\text{NO}_2)_{10}(\text{OH})_4$ into others by the redistribution among them of some of their cobaltous hydroxynitrite. This resolution is attended with another one, that of some of the cobaltous hydroxynitrite into nitrite and hydroxide, the latter retained by the hydroxycobaltinitrite, the former lost to it by undergoing conversion itself to cobaltinitrite in a way similar to the original change. These subsidiary changes may be attributed in part to the force of crystallisation, but are principally to be referred to the feeble hold of the cobaltinitrite upon much cobaltous hydroxynitrite against the tendency of this to become itself cobaltic.

In accordance with the remarkable constitution of Lang's crystalline salt, indicating as it does that atoms of hydroxyl, like nitroxyl groups, can pair together between cobaltic and cobaltous atoms, is the behaviour of the salt when it is acted on by half the quantity of an alkali carbonate equivalent to its cobaltous atoms. Out of 23.7 parts per cent. of cobaltous cobalt present in the salt, 14.1, instead of only 11.85, parts were precipitated in this way.

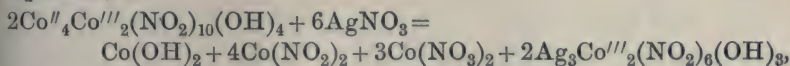
A potassium cobaltous salt is obtained by adding a solution of potassium carbonate, just so long as it continues to cause immediate precipitation, to the solution of cobaltous nitrite after its spontaneous conversion into hydroxycobaltinitrite, filtering, and gradually mixing the red-coloured filtrate with about twice its volume of absolute alcohol. The potassium cobaltous salt is thus obtained as a rose-coloured, flocculent precipitate, which is very soluble in water, and not stable in the air or in solution. Washed with alcohol and dried in a desiccator, it was found to have the

composition expressed by $K_6(NO_2)_6Co''Co'''_2(OH)_8, 5H_2O$. The calculated numbers are for this formula, after deducting $K_{0.3}$ and adding in its place $H_{0.3}$, the salt as prepared showing a deficiency of $1/20$ th of the six atoms of potassium: total cobalt, f. 19.56, c. 19.62; cobaltic cobalt, f. 12.82, c. 13.08; potassium, f. 24.73, c. 24.72; nitrogen, f. 9.36, c. 9.32. Only in the case of the cobaltic cobalt, and then but slightly, do the calculated numbers differ appreciably from the numbers found.

The empirical formula is remarkable in that it can be expanded into $6KNO_2 + Co_3(OH)_8 + 5H_2O$. The constitutional formula of the salt is that of a hexapotassium hydroxycobaltous hydroxycobaltinitrite:



With a dilute solution of silver nitrate, the solution of transformed cobalt nitrite yields a straw-yellow precipitate, which is slightly soluble in water, giving it an orange-yellow colour. It is unstable when moist, changing into silver nitrite and basic cobaltic products. Its composition agrees well with the formula $Ag_3Co'''_2(NO_2)_6(OH)_3$: silver, f. 42.12 and 41.97, c. 42.13; cobalt, f. 15.61 and 15.56, c. 15.35; nitrogen, f. 10.70 and 10.66, c. 10.92. The analyses were made on different preparations of the salt. Sometimes, instead of the salt or with it, silver nitrite and cobaltic precipitates are formed. The simplest equation for expressing the interaction, in which the silver hydroxycobaltinitrite is alone precipitated, is:

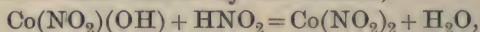


it being understood that the cobaltous hydroxide remains in solution in combination with undecomposed hydroxycobaltinitrite, and that the cobaltous nitrite similarly combines with, or else proceeds to pass of itself into, hydroxycobaltinitrite. The constitutional formula of the silver salt is $(AgNO_2NO_2)_3Co'''_2(OH)_3$.

The three salts which have been obtained in this investigation of the change undergone by cobaltous nitrite in aqueous solution, namely, hydroxycobaltous hydroxycobaltinitrite, potassium hydroxycobaltous hydroxycobaltinitrite, and silver hydroxycobaltinitrite, are not the first of the hydroxycobaltinitrites which have been prepared and examined. But the method of obtaining these others differed from that used in the present work, in that the first step was the dissolution of cobalt carbonate in presence of water by the action of the nitrous gases from nitric acid and arsenious oxide.

By taking the nitrite or carbonate of another metal with the cobalt carbonate, double salts were obtained. The salt of the other metal was taken in the proportion of three equivalents to two of cobalt carbonate, so that, by passing in the nitrous gases long enough, normal cobaltinitrites could be and were thus prepared by Rosenheim and Koppel, who introduced this method of obtaining cobaltinitrites and hydroxynitrites, and prepared several of them for the first time (*Zeitsch. anorg. Chem.*, 1898, **17**, 35). The hydroxycobaltinitrites they obtained and analysed were a cobaltous, a barium, a strontium, a zinc, and a silver hydroxycobaltinitrite, whilst others were met with.

It will be seen that the method followed in preparing these hydroxycobaltinitrites is not well suited for the investigation of the problem which is the subject of the present paper. For, in presence of nitrous acid and nitric peroxide, there will occur some neutralisation of basic nitrite by the former,

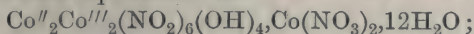


and possibly some production of cobaltic nitrite from cobaltous nitrite and nitric peroxide, $\text{Co}''(\text{NO}_2)_2 + \text{NO}_2 = \text{Co}'''(\text{NO}_2)_3$, whereby the nature of the self-transformation of the cobaltous nitrite becomes obscured and the course of the change interfered with. Another objectionable feature of this mode of preparing hydroxycobaltinitrites is the production of more or less nitrate, which seems unavoidable.

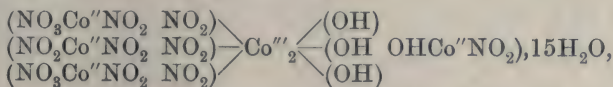
In spite of the comparative unsuitability of their process from the point of view of this paper, it was necessary to repeat, if possible, some of Rosenheim and Koppel's work, the results of which were hardly consistent with those which had been obtained by using the Lang process. The cobaltous salt they have described was apparently indistinguishable from that of which an account is now given in this paper (p. 726) except in composition. A re-examination of the cobaltous salt thus prepared was therefore decided on.

Nitrous gases were passed into water containing cobalt carbonate in suspension until dissolution of the latter was nearly complete. The filtered solution was evaporated under diminished pressure at 30°, and yielded the expected crystals, which were analysed. The results agreed well with Rosenheim and Koppel's, except that the latter did not include any estimation of the cobaltic element, the proportion of it present being assumed by them to be two-fifths of the total cobalt. Calculation for $\text{Co}''_4\text{Co}'''_2(\text{NO}_2)_8(\text{NO}_3)_2(\text{OH})_4, 15\text{H}_2\text{O}$ gives figures which, with those here obtained and those found by Rosenheim and Koppel, are as follows: total cobalt, f. 30.27, c. 29.90; R. and K., f. 30.15; cobaltic cobalt, f. 9.80, c. 9.97; total

nitrogen, f. 11.77, c. 11.82; R. and K., f. 11.65; nitrite nitrogen, f. 9.31, c. 9.46; R. and K., f. 8.90. Rosenheim and Koppel gave the salt a formula equivalent to



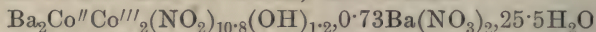
but this can be set aside now that the ratio $\text{Co}'' : \text{Co}'''$ has been experimentally determined. In the light thrown on the constitution of the hydroxycobaltinitrites by the work described in the present paper, the constitution of this nitrate-containing cobaltous salt may be expressed by:



which differs from the formula given on p. 727 only in having 2NO_3 in place of 2NO_2 . But the crystals obtained from the solution prepared by Lang's method were more basic than this, and, in accordance with this difference, it was found that the crystals obtained from the solution prepared by Rosenheim and Koppel's method do not, when treated with solution of sodium carbonate equivalent to half their cobaltous element, give a precipitate containing noticeably more than half the cobaltous element. In the case of the crystals from the Lang solution, the precipitate, similarly obtained, did include much more than this. In that case some, in this case all, of the cobaltous hydroxide remained in solution as a more basic hydroxycobaltinitrite (p. 728).

From the Rosenheim and Koppel solution the same potassium hydroxycobaltous salt and the same silver salt were obtained as from the Lang solution. In the statement on p. 729 the second analysis of the silver salt was made on a precipitate from such a solution. Rosenheim and Koppel failed to obtain from it anything but silver nitrite in this way, although they isolated a different, greyish-brown, microcrystalline, hydrated silver hydroxycobaltinitrite, indirectly, through a zinc hydroxycobaltinitrite prepared in their way. To their silver salt and the other hydroxycobaltinitrites described by them, they have given formulæ equivalent to $\text{Ag}_4\text{Co}'''_2(\text{NO}_2)_6(\text{OH})_4 + \text{H}_2\text{O}$, $\text{Ba}_2\text{Co}'''_2(\text{NO}_2)_8(\text{OH})_2 + 0.2\text{Co}(\text{NO}_3)_2 + 11\text{H}_2\text{O}$, $\text{Sr}_2\text{Co}'''_2(\text{NO}_2)_8(\text{OH})_2 + 10\text{H}_2\text{O}$, $\text{Zn}_2\text{Co}'''_2(\text{NO}_2)_6(\text{OH})_4 + 9\text{H}_2\text{O}$. But more evidence is wanted to carry conviction as to the existence of such differences as those presented between the formulæ of the strontium and zinc salts and between the composition of Rosenheim and Koppel's series of salts and that of the salts now described. There is no evidence recorded in their paper as to whether the presence of additional nitrogen as nitrate was tested for in any other case than that of the barium salt, although in all cases the mother liquor of the salt contained nitrate. Also, evidence is

wanting of the proportion of cobaltic element in the salts. As a consequence of the latter omission in the paper and by taking the more probable view that the nitrate in the barium salt was that of barium rather than of cobalt, the formula



can be given to their second preparation of the barium salt, and with markedly closer approximation to the results of analysis than that reached by their formula. Their silver salt, in which it is improbable that either cobaltous metal or nitrate was present, may have its given formula so rearranged as to make it appear as a derivative of the silver salt, $(\text{AgNO}_2\text{NO}_2)_3\text{Co}'''_2(\text{OH})_3$, here described, thus: $(\text{AgNO}_2\text{NO}_2)_3\text{Co}'''_2(\text{OH})_3(\text{OH})\text{Ag}, \text{H}_2\text{O}$.

It has not been possible to find time and opportunity to extend this research by further work on Rosenheim and Koppel's solution and its derived hydroxynitrites, or on Lang's solution; but enough has been accomplished, probably, to justify the expectation that all hydroxycobaltinitrites will prove to be of the type of the salts met with in this investigation.

The author is greatly indebted to Professor T. Haga for valuable advice given him during the course of this work, and to Professor E. Divers, F.R.S., for assistance in expressing the significance of the results of the experiments and in preparing the text of the paper.

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L.—*The Rate of Hydration of Acetic Anhydride.*

By ALBERT CHERBURY DAVID RIVETT (Rhodes Scholar) and
NEVIL VINCENT SIDGWICK.

THE solubility in water of acetic anhydride as such was pointed out by Hinsberg (*Ber.*, 1890, **23**, 2962), and later by Lumière and Barbier (*Bull. Soc. chim.*, 1905, [iii], **33**, 783), who made use of it to bring about certain acetylations in aqueous solution.

An attempt was made by Menshutkin and Vasilieff (*J. Russ. Phys. Chem. Soc.*, 1889, **21**, 188) to determine the rate at which the anhydride combined with water in acetic acid solution, but the results were not satisfactory. The same may be said of the work of Benrath (*Zeitsch. physikal. Chem.*, 1909, **67**, 501), who endeavoured to measure this rate (in acetic acid) by means of the

change of density. Only one experiment was made, in which the remarkable result was obtained that with equivalent quantities of anhydride and water the reaction was unimolecular; that is, that it depended on the concentration of only one of the reacting substances.

Lumière and Barbier, in a second paper (*Bull. Soc. chim.*, 1906, [iii], 35, 625), modified the method of Menshutkin and Vasilieff, and applied it to solutions of the anhydride in water. Their procedure was to act on the mixture after the lapse of a certain time with aniline, when the anhydride was at once precipitated as acetanilide, with the liberation of an equivalent of acid. The total acid present was then determined by titration with alkali. They carried out two experiments at 0° , and two at 15° . They deduce no velocity constant; but if their results are calculated on the unimolecular formula, an approximation to constancy is obtained, and the value appears to diminish with increase of concentration.

We have endeavoured to determine the constant with greater accuracy by means of the conductivity. If we start with a solution of the anhydride in water, the conductivity at any moment is due solely to the amount of acetic acid formed; and the only way in which the presence of the unchanged anhydride is likely to affect it is by its influence on the viscosity of the solution. It is probable that the ionic velocity is inversely proportional to the viscosity of the medium, so long as this is not too great. This appears from the work of Hartley, Thomas, and Applebey (*Trans.*, 1908, 93, 538); Green (*ibid.*, 2049), who arrived at a different conclusion, used solutions of a much higher viscosity. The accurate measurement of the viscosity at 25° of a solution of acetic anhydride in water is not possible on account of the rapidity of the hydration, and the rise of temperature accompanying it. Rough experiments indicated that the viscosity did not change much during the reaction, and this result was confirmed by more accurate determinations at 0° , where the velocity of change may be expected to be about a tenth of that at 25° , so that half the anhydride is hydrated after fifty minutes. The solution of the anhydride in water was placed in an Ostwald viscometer at 0° , and the time of flow measured after successive intervals, until the conversion into acid was complete. Table I gives the time in minutes from the addition of the anhydride to the beginning of the flow, and the time of flow in seconds. The results show a slight initial tendency to rise, but the change is not so much as 1 per cent., and this may be partly or wholly due to the rise of temperature caused by the reaction. We may therefore assume that the

viscosity of an aqueous solution of acetic anhydride is the same as that of the acetic acid solution which it produces. This is remarkable, since the viscosity of the pure anhydride (referred to water) is about 0.94, whilst that of the pure acid is 1.34.

TABLE I.

<i>Experiment 1.</i>		<i>Experiment 2.</i>	
Time from mixture (minutes).	Time of flow (seconds).	Time from mixture (minutes).	Time of flow (seconds).
6	388.3	5	417.6
36	389.2	37	418.3
73	389.1	85	419.8
112	389.0	150	420.7
172	389.4	181	420.5
206	389.2	213	420.3
Normality	0.35	Normality	0.53
Viscosity (referred to water)	1.04	Viscosity	1.06

The conductivity of the acetic acid solutions was determined in cells of the usual Ostwald form; the water was obtained from a still of the pattern described by Hartley, Campbell, and Poole (Trans., 1908, **93**, 428); its conductivity varied from 0.6 to 1.5×10^{-6} mhos. The published measurements of the conductivity of acetic acid solutions show considerable discrepancies, and it seemed better to make new determinations under conditions similar to those obtaining in the velocity measurements.

The results are given in table II, and these are plotted against the cube root of the concentration in curve A, Fig. 1.

TABLE II.

Specific Conductivity of Acetic Acid at 25°.

Normality.	Sp. cond.	Normality.	Sp. cond.
2.9771	1.854	0.1982	0.7304
2.0060	1.789	0.1861	0.7079
1.4886	1.671	0.1760	0.6918
1.3374	1.620	0.1321	0.5983
1.0029	1.474	0.1206	0.5653
0.8917	1.415	0.0930	0.4986
0.7443	1.321	0.0804	0.4623
0.6687	1.264	0.05873	0.4033
0.5945	1.205	0.04020	0.3372
0.4458	1.066	0.02686	0.2749
0.3964	1.010	0.01791	0.1146
0.3722	0.9722	0.01194	0.1830
0.2973	0.8832	0.00799	0.1494
0.2643	0.8401	0.00483	0.1145

The viscosities were measured in two Ostwald viscometers kindly lent by Mr. H. B. Hartley. Their times of flow for water were between three and four minutes. The densities were determined in an ordinary pyknometer of about 15 c.c. capacity. The values of

the densities and viscosities (referred to water at 25°) are given in table III, and the viscosities are plotted against the concentrations in curve B, Fig. 1.

FIG. 1.

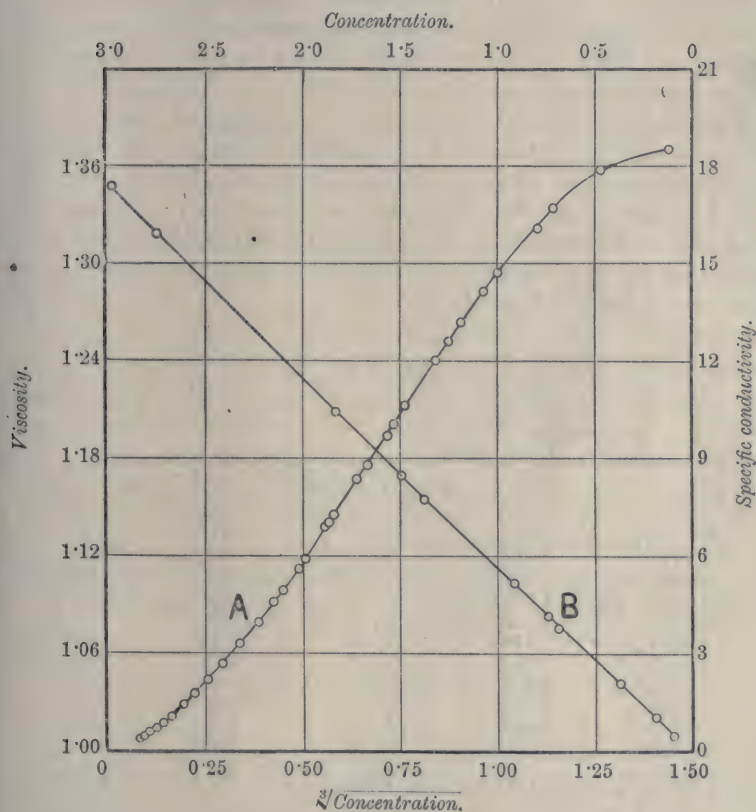


TABLE III.

Density and Viscosity of Acetic Acid at 25°.
(Referred to water at 25° as unity.)

Normality.	Density.	Viscosity.
2.977	1.0235	1.347
2.746	1.0217	1.319
1.831	1.0148	1.208
1.489	1.0121	1.169
1.373	1.0112	1.154
0.9154	1.0076	1.103
0.7443	1.0061	1.082
0.6865	1.0056	1.075
0.3722	1.0032	1.042
0.1861	1.0018	1.021
0.0930	1.0010	1.010

From the curves for the conductivity and the viscosity, values were interpolated for a regular series of concentrations. The product of the conductivity and the viscosity was then plotted against the concentration, on scales increasingly open as the concentration diminished, and these curves were used for the interpolations required in the velocity experiments, in which the conductivity values were multiplied by the viscosity corresponding to the final normality of the acid.

It seemed interesting with these figures at hand to ascertain what difference in the applicability of Ostwald's dilution law was made by the introduction of the viscosity correction. In table IV, the second column gives the molecular conductivities (μ) interpolated for a series of normalities, n , and the third ($\mu\eta$) the same values multiplied by the viscosities. The constants given under K are calculated from the formula:

$$k = \frac{\mu^2 n}{\mu_\infty (\mu_\infty - \mu)} \times 10^5,$$

and those under K' from a similar formula with $\mu\eta$ substituted for μ : μ_∞ was taken as 392.4.

TABLE IV.

Normality.	μ .	$\mu\eta$.	K .	K' .
2.744	0.675	0.890	0.81	1.42
2.000	0.905	1.112	1.07	1.61
1.405	1.195	1.385	1.31	1.76
0.9412	1.571	1.736	1.52	1.85
0.4565	2.370	2.494	1.67	1.86
0.2941	3.034	3.133	1.77	1.89
0.2107	3.604	3.689	1.79	1.88
0.0429	8.070	8.103	1.85	1.87
0.0313	9.520	9.552	1.89	1.90
0.00926	17.36	17.38	1.90	1.90

It will be seen that approximate constancy in K is reached at a normality of about 0.05, while in K' equal constancy begins at about 0.95. Rudolf (*Zeitsch. physikal. Chem.*, 1903, **43**, 274), using a more complicated formula to correct for viscosity, obtained agreement at a normality of 0.6.

Velocity Experiments.

The cell found most convenient for this work was in the shape of a stoppered flask, of volume about 100 c.c., with electrodes sealed in; 70 c.c. of solution were used for every experiment. The acetic anhydride was obtained from Kahlbaum as specially pure and free from homologous anhydrides. Its purity for our purpose was tested by dissolving various quantities in water, keeping them overnight, and then determining the acidity and the conductivity

of the resulting solutions. The values were found to agree with those obtained for the pure acid. The method of procedure in the velocity experiments was as follows. To 70 c.c. of water contained in a Jena flask and warmed in the thermostat to 25°, the approximately correct amount of anhydride was added. The mixture was at once violently shaken, fall of temperature being avoided by conducting the shaking as far as possible in the bath. When the anhydride was completely dissolved, the solution was poured into the cell, and the readings on the bridge begun, the times from the moment of adding the anhydride being recorded (to the nearest second) by another observer. During the experiment the solution was several times shaken round in the cell, in order to minimise the heat effect. As a rule, no measurements were taken after fifteen to twenty minutes, and the end-point could safely be read after one or two hours, although the stronger solutions were always given a longer time. The concentrations employed varied between 0.02 and 1.07 normal, the normality in this, as in all cases, being referred to the acid produced, and thus being the equivalent normality of the anhydride. The first two experiments in table V show in detail the results obtained with a weaker and a stronger solution, and may be regarded as typical of the rest. In the third experiment (31) in this table, the anhydride was not dissolved in water, but in acetic acid of normality 0.828; the bearing of this result will be discussed later.

In this table the column k is calculated on the unimolecular formula:

$$k = \frac{1}{t} \log. \frac{A}{A-x},$$

where t is the time in seconds, and A the initial concentration, and x that at time t of the anhydride. If the rate of change is proportional to the product of the concentrations of the anhydride and the water, then k represents the real constant multiplied by the constant concentration of the water. To regard the water-concentration, even in the stronger solutions, as constant, probably does not introduce an error greater than that due to the method of experiment.

This experimental error is mainly occasioned by (1) the uncertainty as to the initial time; (2) the heat developed as a result of the reaction; (3) the fall of temperature during part of the shaking, and during the transfer from the flask to the cell; and (4) the inaccuracy due to the rapidity with which the bridge-measurements have to be made. Of these, (2) and (3) are in opposite directions, and will probably tend to balance one another in the stronger solutions. The time was always taken from the

TABLE V.

<i>Experiment 9.</i>			<i>Experiment 21.</i>		
0.37 c.c. anhydride.			1.78 c.c. anhydride.		
<i>t.</i>	<i>x.</i>	<i>k.</i>	<i>t.</i>	<i>x.</i>	<i>k.</i>
87	0.02378	0.001146	114	0.1334	0.001105
94	0.02548	0.001147	121	0.1405	0.001106
108	0.02835	0.001125	130	0.1487	0.001100
115	0.02973	0.001117	138	0.1554	0.001092
124	0.03168	0.001118	145	0.1621	0.001093
132	0.03375	0.001129	154	0.1693	0.001085
141	0.03553	0.001125	168	0.1804	0.001076
148	0.03703	0.001127	176	0.1870	0.001074
178	0.04300	0.001130	184	0.1932	0.001070
187	0.04433	0.001117	208	0.2116	0.001064
194	0.04568	0.001121	217	0.2172	0.001055
228	0.05153	0.001118	228	0.2249	0.001052
238	0.05313	0.001117	237	0.2329	0.001061
282	0.05985	0.001116	249	0.2405	0.001055
305	0.06350	0.001129	259	0.2480	0.001058
323	0.06578	0.001126	310	0.2799	0.001052
339	0.06798	0.001130	326	0.2893	0.001052
363	0.07090	0.001130	346	0.3008	0.001068
383	0.07325	0.001130	374	0.3160	0.001053
417	0.07748	0.001149	392	0.3260	0.001058
437	0.07880	0.001130	422	0.3421	0.001067
473	0.08253	0.001141	455	0.3559	0.001063
504	0.08528	0.001146	486	0.3695	0.001068
544	0.08848	0.001149	524	0.3852	0.001076
587	0.09100	0.001136	563	0.4010	0.001090
629	0.09340	0.001129	607	0.4115	0.001072
693	0.09690	0.001130	652	0.4265	0.001088
760	0.10010	0.001135	718	0.4430	0.001093
852	0.10360	0.001140	809	0.4620	0.001102
			953	0.4810	0.001085
Mean.....		0.001131	Mean.....		0.001075
$A=0.1160.$			$A=0.5300.$		

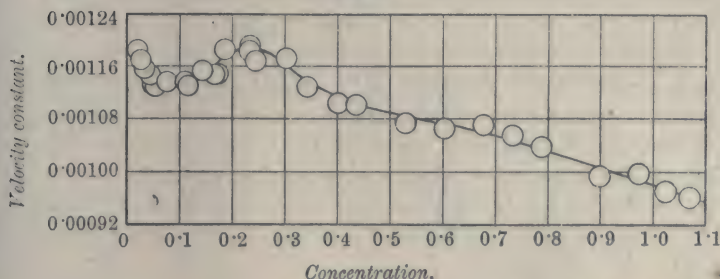
Experiment 31.—In presence of acetic acid.

<i>t.</i>	<i>x.</i>	<i>k.</i>	<i>t.</i>	<i>x.</i>	<i>k.</i>
54	0.065	0.000981	349	0.303	0.000954
62	0.074	0.000981	365	0.310	0.000944
70	0.082	0.000971	380	0.323	0.000967
77	0.088	0.000953	423	0.342	0.000952
135	0.145	0.000952	443	0.353	0.000958
150	0.160	0.000962	491	0.373	0.000952
162	0.173	0.000978	542	0.395	0.000959
175	0.184	0.000976	1171	0.524	0.000965
207	0.208	0.000961	1505	0.545	0.000951
218	0.217	0.000963			
220	0.226	0.000962			
245	0.236	0.000956			
258	0.244	0.000950			
275	0.257	0.000956			
286	0.265	0.000959			
318	0.286	0.000961			
333	0.293	0.000951			
			Mean.....		0.000960
			Initial concentration of:		
			Acid		0.828
			Anhydride (= A)...		0.566
			(x =concentration of acid formed from anhydride.)		

moment when the anhydride had been added and the shaking begun. It will be seen that it is difficult to give a precise estimate of the magnitude of the experimental error.

In table VI are given the mean values of the constant obtained in a series of some thirty experiments at different concentrations. The results are plotted in Fig. 2, where the radius of the circle drawn round each point represents approximately a departure of

FIG. 2.



1.5 per cent. on either side of the experimental mean value. This is perhaps a somewhat low estimate of the probable error.

TABLE VI.

Expt.	Concentration.	<i>k</i> .	Expt.	Concentration.	<i>k</i> .
1	0.02015	0.001186	16	0.2449	0.001169
2	0.02640	0.001171	17	0.3028	0.001173
3	0.03307	0.001157	18	0.3425	0.001130
4	0.04563	0.001147	19	0.4010	0.001105
5	0.04883	0.001133	20	0.4355	0.001103
6	0.05433	0.001130	21	0.5300	0.001075
7	0.07575	0.001137	22	0.6040	0.001067
8	0.1115	0.001137	23	0.6785	0.001072
9	0.1160	0.001131	24	0.7345	0.001056
10	0.1441	0.001154	25	0.7895	0.001039
11	0.1670	0.001148	26	0.8995	0.000994
12	0.1734	0.001149	27	0.9745	0.001002
13	0.1949	0.001186	28	1.0255	0.000971
14	0.2339	0.001184	29	1.0705	0.000961
15	0.2348	0.001192			

There is no obvious way of accounting for the irregularity at the dilute end of the curve, but considering the number of experiments carried out at the lower concentrations, and the agreement of the results, it is impossible to avoid the conclusion that the irregularity is real.

The conductivity of the water will not account for the rise of the curve at the dilute end, not only because the error from this cause is small, but also because water of the same degree of purity

was used in obtaining the original curve for the conductivity of acetic acid.

The falling off of the constant in strengths above 0.2 normal may be due in part to the viscosity of the solution, but the decrease of the constant is somewhat greater than the increase of viscosity.

In this connexion two experiments conducted in the presence of a considerable amount of acetic acid, one of which (Experiment 31) has already been given in table V, are of interest. In these cases the earlier conductivities were plotted on a curve, and the value at $t=100$ was found by interpolation. This time was taken as zero, and the corresponding concentration was subtracted from the value given by each measurement in order to obtain x . In the first experiment it was found that with an initial concentration of acid 0.302 normal, the velocity constant for 0.2104 normal anhydride, which in the absence of this acid would have been 0.00118, was 0.00110; if the whole had been present as anhydride (normality 0.512), it would have been about 0.00109. The second experiment (quoted above) showed that the constant for 0.566 normal anhydride, which in pure water is about 0.00107, is lowered by the initial presence of 0.828 normal acid to 0.00096.

It is quite evident from this curve, from the agreement of the constants in each experiment, and from the two experiments just mentioned, that the hydrogen ion produced in the reaction exerts no positive catalytic influence. The concentration of acetic acid in the whole series of experiments varies from 0.02 to 1.07, and if we include the experiments with initial acid rises to 1.39; that is, it varies in the ratio of 1 to 53 and 70 respectively. The concentration of the hydrogen ion is nearly proportional to the square root of that of the total acid, and hence this rises in the ratio of 1 to 7 or 8. On the nearest analogy available, that of the hydrolysis of esters (and, we may add, of amides), we should expect the velocity constant to be proportional to the concentration of the hydrogen ion, and hence to rise with the concentration of the anhydride to something like eight times its original value, instead of which it falls about a fifth. We must therefore conclude that the mechanism of the hydration of acetic anhydride is quite different from that of the hydrolysis of an ester, and that the hydrogen ion plays no part in it. It will be interesting to see whether steric hindrance, which delays all the reactions of acid derivatives which are catalysed by hydrogen ion, has any influence in the hydration of anhydrides.

Summary.

1. The conductivities and viscosities at 25° of aqueous solutions of acetic acid from 3 normal downwards have been measured.

2. If we assume the ionic velocity to be inversely proportional to the viscosity, Ostwald's dilution law holds up to a normality of 0.94, whereas in its simple form it holds only up to 0.05.

3. Using these measurements, the rate of hydration of acetic anhydride in water at 25° was measured by means of the conductivity. It was found to proceed in accordance with the unimolecular law; it is not catalysed by hydrogen ion, and beyond a certain point the constant falls steadily with increasing concentration.

The work is being extended to other anhydrides. We wish to thank Mr. J. J. Manley for assistance in many ways during the course of the research.

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LI.—3-Aminoquinoline and the Colour of its Salts.

By WILLIAM HOBSON MILLS and WALTER HENRY WATSON.

OF the seven possible amino-derivatives of quinoline, six have already been described. The hitherto unknown 3-derivative seemed to merit investigation from more than one point of view.

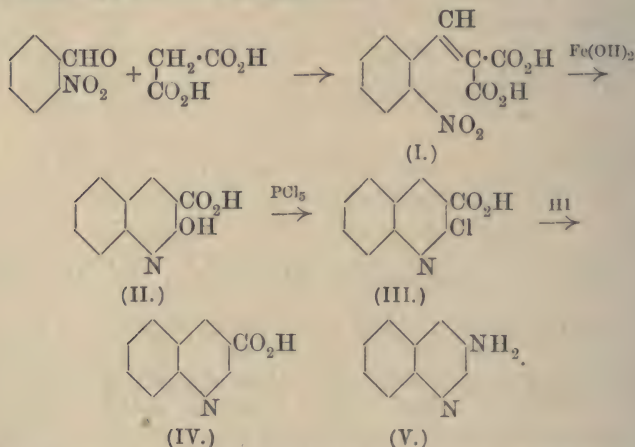
The four aminoquinolines in which the amino-group is attached to the benzene ring are diazotisable. Moreover, they form coloured salts, and the metallic salts of the corresponding hydroxy-compounds (with the possible exception of the 5-derivative) also show colour or fluorescence.

On the other hand, of the two already known aminoquinolines in which the amino-group is attached to the pyridine nucleus, the 4-derivative does not give rise to diazonium salts (Claus and Frobenius, *J. pr. Chem.*, 1897, [ii], 56, 191; Wenzel, *Monatsh.*, 1894, 15, 458), and although the behaviour of the 2-derivative towards nitrous acid does not appear to have been investigated, the same is almost certainly true of it on account of the close analogy in other respects of the 2- and 4-derivatives of quinoline to one another and to the

corresponding derivatives of pyridine. Moreover, the salts of these two substances are also colourless, and this is likewise the case with those of the corresponding hydroxy-compounds.

It appeared, therefore, of interest to determine in what manner 3-aminoquinoline, in which the amino-group, although attached to the pyridine nucleus, would yet be less directly under the influence of the ring nitrogen, would behave towards nitrous acid, and, secondly, in connexion with the origin of the colour of the salts of amino- and hydroxy-quinolines, whether or not the salts of these unknown 3-derivatives would be coloured.

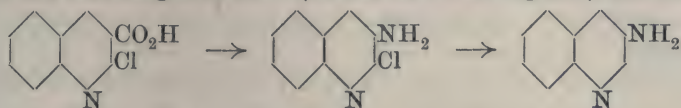
On reviewing the possible methods of obtaining this base, it appeared that it would probably be most readily prepared from quinoline-3-carboxylic acid by the replacement of the carboxyl by the amino-group, provided that some convenient method could be discovered for the preparation of this acid, since hitherto it has been a somewhat difficultly accessible compound.



We found that it could be satisfactorily prepared by the reduction by means of hydriodic acid and phosphorus of 2-chloroquinoline-3-carboxylic acid (III). This may be obtained by the action of phosphorus pentachloride (Friedländer and Göhring, *Ber.*, 1884, **17**, 460) on carbostyrylcarboxylic acid (II), and this in turn is easily prepared by the reduction of the condensation product (I) of *o*-nitrobenzaldehyde and malonic acid (Stuart, *Trans.*, 1885, **47**, 155; 1888, **53**, 143; H. Meyer, *Monatsh.*, 1908, **28**, 47). The final step in the synthesis of the base, namely, the replacement of the carboxyl in the acid (IV) by the amino-group, can be brought about without difficulty in the usual manner by treating the corresponding amide with sodium hypobromite.

The alternative course of replacing the carboxyl by the amino-

group before elimination of the chlorine was also tried, but was found to be less advantageous, since (as was to be anticipated) the chlorine



atom was less readily removable from the amino- than from the carboxyl derivative (compare Mills and Widdows, *Trans.*, 1908, **93**, 1376).

The new base exists in two modifications. As first obtained, crystallised from toluene, it melted at 84° . Suddenly in the course of our experiments the melting point rose to 94° , and for some time the form melting at the lower temperature was never again obtained. It was, however, at length discovered that after the modification melting at 94° has been fused in a melting-point tube, the resolidified substance melts sharply at 84° , and that when a minute fragment of the original solid is allowed to fall into the resulting liquid at a slightly higher temperature, it resolidifies and then melts at 94° . This observation, which was repeated on a larger scale, suggested that the production of the 94° modification was due to inoculation by particles present in the laboratory dust, and that this is actually the case was proved by the fact that, when such inoculation is guarded against, the base crystallises constantly from toluene in the form melting at 84° . An interesting confirmation of this is that after the summer vacation it was found to crystallise from toluene in this form when no precautions were taken, and it did so invariably in another laboratory which had not become infected.

The crystals which separate from aqueous or aqueous-alcoholic solutions, however, appear always to melt at 94° , even when crystallisation takes place under sterile conditions. It is probably through recrystallisation of a sample in this manner that infection of the laboratory was originally brought about.

These observations are of interest in connexion with the experiments of Biilmann (*Ber.*, 1909, **42**, 182, 1444) and Liebermann (*Ber.*, 1909, **42**, 1027, 4659) on the modifications of *allocinnamic acid*.*

3-Aminoquinoline is readily diazotised. The resulting diazonium salt couples in the normal manner with β -naphthol in alkaline solution, forming quinoline-3-azo- β -naphthol. The solution of the diazonium sulphate when heated evolves nitrogen, and on cooling deposits crystals of the sulphate of 3-hydroxyquinoline.

The salts which 3-aminoquinoline forms with one equivalent of acid

* References to the effects of inoculation have also been made by Miers and Isaac (*Proc. Roy. Soc.*, 1907, **79**, A, 328; *Min. Mag.*, 1908, **15**, 39) and by Baxter and Tilley (*Amer. Chem. J.*, 1909, **31**, 201).

are intensely yellow, both in the solid state and in solution. They also show strong, blue fluorescence in dilute solution. However, the salts of the 2-chloro-base are, on the other hand, quite colourless. Moreover, 3-aminoquinaldine has recently been described by Stark (*Ber.*, 1907, **40**, 3428), but it does not appear from his description that solutions of its salts are coloured, although he emphasises their intense fluorescence.

The base, therefore, shows fairly complete agreement in properties with the *Bz*-aminoquinolines, and the exceptional character of aminoquinolines with the amino-group in the pyridine ring seems to be confined, analogously to the derivatives of pyridine itself, to the 2- and 4-derivatives.

The closer study of the colour of the salts of the base has led to interesting results. If the effect of gradually adding acid to the solution of a fixed quantity of base is examined colorimetrically, and coefficients of extinction are plotted as ordinates against the equivalent proportions of hydrochloric acid present as abscissæ, remarkable curves are obtained, from which it appears that the intensity of the colour of the solutions is at a maximum at a point just beyond that at which the amount of hydrochloric acid corresponds with the composition $(C_9H_8N_2)_2.HCl$. Further addition of acid brings about a rapid diminution of colour, a minimum occurring when the composition of the normal salt, $(C_9H_8N_2).HCl$, has been reached, the colour intensity then being only about 50 per cent. of that of the half-neutralised base. The explanation of this phenomenon that first suggests itself is that it is due primarily to the formation of complex salts in the solution of the type $(C_9H_8N_2)_2.HCl$. Since it was possible to obtain unmistakable evidence that such salts actually exist, we conclude that this explanation is the correct one.

We are not aware that the formation of complexes of this nature has been previously observed in the case of organic bases, although it is well known that hydroxylamine forms compounds of the kind, for example, $(NH_2OH)_2.HCl$ (Lossen, *Annalen*, 1871, **160**, 242), $(NH_2OH)_3.HI$ (Dunstan and Goulding, *Trans.*, 1896, **69**, 1839).

A somewhat similar phenomenon was observed by Baly and Miss Marsden in the case of alcoholic solutions of amino-aldehydes and -ketones of the aromatic series (*Trans.*, 1908, **93**, 2108).

EXPERIMENTAL.

Quinoline-3-carboxylic Acid.

The chloroquinolinecarboxylic acid, which may be regarded as forming the starting point in this investigation, was prepared in the manner indicated in the introduction.*

It was converted into quinoline-3-carboxylic acid by boiling it in quantities of 10 grams for two hours with hydriodic acid, D 1·7 (25 c.c.), red phosphorus (3 grams), and potassium iodide (3 grams). On cooling, an abundant crystallisation of the yellow hydriodide of the acid took place. This was collected and the filtrate concentrated, when a further crop of crystals was obtained. The hydriodide was decomposed by warming with an excess of aqueous potassium hydroxide, and the quinolinecarboxylic acid precipitated by acidifying with acetic acid. Some elimination of the carboxyl group apparently takes place during the reduction, since the filtrate always contains a little quinoline. The acid was purified by dissolving in hot dilute sulphuric acid, filtering from a little insoluble substance, which appears to be hydroxy-acid, and re-precipitating. The yield is about 75 per cent. of the theoretical. After recrystallising from alcohol, it formed a white solid, melting at 275°, and otherwise corresponding with the description given by previous investigators.

Quinoline-3-carboxamide.

On mixing the dry acid (10 parts) with phosphorus pentachloride (12 parts), both finely powdered, a considerable rise of temperature occurred, but no hydrogen chloride was evolved. After heating on the water-bath for an hour, the product was cooled and added in small quantities at a time to an ice-cold and nearly saturated solution of ammonia, when the amide separated as a white solid. After remaining an hour at the ordinary temperature, it was collected and recrystallised from hot water. The yield is about 80 per cent. of the theoretical.

The pure amide forms slender needles melting at 198—199°, and is fairly soluble in alcohol. It is readily hydrolysed on warming with sodium hydroxide to ammonia and quinoline-3-carboxylic acid :

0·1348 gave 19·6 c.c. N_2 (moist) at 20° and 755 mm. $N = 16·53$.

$C_{10}H_8ON_2$ requires $N = 16·28$ per cent.

* Friedländer and Göhring (*loc. cit.*) state that this compound melts at 200°. On account of the readiness with which it decomposes with carbon dioxide and chloroquinoline, it has no sharp melting point. Heated in the usual manner, it begins to soften at about 204°, darkens, and does not completely liquefy until nearly 240°.

3-Aminoquinoline.

A hypobromite solution was prepared by adding bromine (10 grams) to a cold solution of potassium hydroxide (50 grams) in water (950 c.c.). To this liquid the finely-powdered amide (11 grams) was slowly added with constant stirring. Nearly all dissolved, solution being completed by gently warming, after which the liquid was heated to 70° for a few minutes. The solution was then acidified with acetic acid, cooled, and filtered from a little dark-coloured precipitate. The filtrate was made strongly alkaline with sodium hydroxide, and extracted four times with chloroform (500 c.c.). The chloroform solution was dried with ignited sodium sulphate, evaporated, and the brown residue crystallised from toluene, when about 7.5 grams of the amine were obtained from each 11 grams of the amide. The amine was purified by distillation in a vacuum in an Anschütz flask and subsequent recrystallisation from toluene:

0.1800 gave 0.4919 CO₂ and 0.0905 H₂O. C = 74.53; H = 5.59.

0.1116 „ 18.6 c.c. N₂ at 19° and 758 mm. N = 19.55.

C₉H₈N₂ requires C = 75.00; H = 5.55; N = 19.44 per cent.

3-Aminoquinoline is a colourless, crystalline solid, slightly soluble in cold water. In hot water it is moderately soluble, and on cooling the amine separates first as an oil, but from dilute solutions it often forms slender, thread-like aggregations. It is readily soluble in ether, chloroform, or alcohol, and crystallises well from solution in aqueous alcohol or toluene.

The relationships between the two modifications of the base, melting at 94° and 84° respectively, have been described in the introduction (p. 743). To obtain the latter after the laboratory had become infected with the stable form, the flask containing the boiling toluene solution of the substance was heated up to the lip by the hot vapour and immediately closed by a cork pierced by a tube containing a long cotton-wool plug and a toluene seal, all heated to 110°. Experiments carried out less carefully occasionally failed.

The stable modification is easily obtained from solution in toluene in crystals of considerable size. The metastable form crystallises in rosettes of thin, prismatic plates. Both modifications have been examined crystallographically by Dr. G. F. Herbert Smith, of the British Museum, and the authors wish to express to him their best thanks. The following details are taken from his report.

Stable Modification.—The crystals have the form of flat plates, and belong to the sphenoidal class of the orthorhombic system. The large face was selected as the macropinakoid, and was made the pole of reference in all the measurements made:

$$a : b : c = 1.6350 : 1 : 0.9870.$$

Forms present : $a\{100\}$, $m\{110\}$, $b\{010\}$, $e\{011\}$, $d\{101\}$, $p\{111\}$, $r\{211\}$, d and r being rare.

Measurements from $a\{100\}$.

Form.	Calculated values.		Observed values.		No.	Limits of observations.	
	Azimuth.	Distance.	Azimuth.	Distance.		Azimuth.	Distance.
d (101)	90° 0'	58° 53'	*	58° 37'	1	—	—
e (011)	45 22½	90 0	*	*	5	45° 12'—45° 30'	90° 15'
p (111)	—	66 45½	—	66 43	5	—	66° 30'—67° 0'
r (211)	—	49 20	—	49 14	1	—	—
b (010)	0 0	90 0	*	*	—	—	—
m (110)	—	58 33	—	*	17	—	57 54—58 51

There is a distinct cleavage parallel to $b\{010\}$. If a cleavage plate is examined in convergent light, an interference figure of the biaxial type is seen, and the acute bisectrix is therefore at right angles to $b\{010\}$. The sign of the birefringence is negative, and the plane of the optic axes is parallel to the base $\{001\}$, the obtuse bisectrix being therefore at right angles to the large face $a\{100\}$. Refractive indices : α 1.535, β 1.873, γ 1.893, $2E = 40^\circ \text{Li}$, 45°Na , 50°Ti (observed).

Metastable Modification.—Crystalline system.—Monoclinic :

$$a : b : c = 2.2130 : 1 : 1.2889 ; \beta = 90^\circ.$$

Forms present : $\{100\}$, $\{101\}$, $\{110\}$, $\{203\}$.

The following approximate measurements were obtained :

100 : 101	59° 47'	(5)
100 : 110	65 41	(3)
102 : 203	68°—70°	(68° 47') calc.

If the large face is examined in convergent light, an interference figure, which is probably that at right angles to the acute bisectrix, is seen on the edge of the field. If this direction is the acute bisectrix, the plane of the optic axes is parallel to the edge of the prism, the axial angle is very large, and the double refraction is negative in character. The bisectrix makes an apparent angle of 40° with the normal to the large face in the obtuse angle between the latter and the normal to the second prism form.

For comparison with the stable form, the axes b and c should be interchanged, giving the ratio $a : b : c = 1.7170 : 1 : 0.7759$.

3-Aminoquinoline forms colourless solutions, which exhibit a slight blue fluorescence. This becomes much more intense on the addition of an acid, even carbonic, and the solution turns yellow.

Salts of 3-Aminoquinoline.

The *monohydrochloride*, $\text{C}_9\text{H}_8\text{N}_2\text{HCl}$, is precipitated on passing hydrogen chloride into an alcoholic solution of the base, or on dissolving the base in an equivalent of 3*N*-hydrochloric acid, adding another equivalent of strong acid, and allowing to remain. It is most

conveniently analysed by titration with *N*/10-sodium hydroxide solution, the end point being sharply indicated by the disappearance of the colour and the strong fluorescence :

0.1850 required 10.3 c.c. *N*/10-NaOH. $\text{HCl} = 20.30$.

$\text{C}_9\text{H}_8\text{N}_2 \cdot \text{HCl}$ requires $\text{HCl} = 20.20$ per cent.

The *dihydrochloride*, $\text{C}_9\text{H}_8\text{N}_2 \cdot 2\text{HCl}$, was obtained by the addition of a large excess of alcoholic hydrogen chloride to an alcoholic solution of the amine. The salt had a pale yellow colour, due probably to the presence of a little monohydrochloride, as is indicated by the analysis :

0.1968 required 17.7 c.c. *N*/10-NaOH. $\text{HCl} = 32.74$.

$\text{C}_9\text{H}_8\text{N}_2 \cdot 2\text{HCl}$ requires $\text{HCl} = 33.58$ per cent.

The *platinichloride*, $(\text{C}_9\text{H}_8\text{N}_2)_2 \cdot \text{H}_2\text{PtCl}_6$, separates as a heavy yellow precipitate when a solution of platinic chloride is added to one of the hydrochloride of the base containing an excess of hydrochloric acid. A specimen of the salt dried at the ordinary temperature did not lose weight on heating at 100° :

0.4044 gave 0.1124 Pt. $\text{Pt} = 27.79$.

$(\text{C}_9\text{H}_8\text{N}_2 \cdot \text{HCl})_2 \cdot \text{PtCl}_4$ requires $\text{Pt} = 27.91$ per cent.

The *picrate*, $\text{C}_9\text{H}_8\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, is a sparingly soluble, bright yellow salt, which readily dissociates in solution. It is best obtained by dissolving the amine in aqueous alcohol and adding a slight excess of picric acid. Specimens of the picrate, dried in a vacuum, were analysed by reduction with a standard solution of titanium chloride (Knecht and Hibbert, *Ber.*, 1903, 36, 1554) :

0.0508 contained 0.0312 $\text{C}_6\text{H}_3\text{O}_7\text{N}_3 = 61.38$.

$\text{C}_9\text{H}_8\text{N}_2 \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$ requires $\text{C}_6\text{H}_3\text{O}_7\text{N}_3 = 61.40$ per cent.

The *chromate*, $2\text{C}_9\text{H}_8\text{N}_2 \cdot \text{H}_2\text{CrO}_4$, is obtained as a deep yellow precipitate on the addition of potassium chromate to a solution of the acetate of the base. It is slightly soluble in cold water, and undergoes some decomposition when the solution is heated :

0.4266 gave 0.1282 Cr_2O_3 . $\text{CrO}_3 = 39.53$.

$2\text{C}_9\text{H}_8\text{N}_2 \cdot \text{H}_2\text{CrO}_4$ requires $\text{CrO}_3 = 39.55$ per cent.

The Colour of Solutions of Salts of 3-Aminoquinoline.

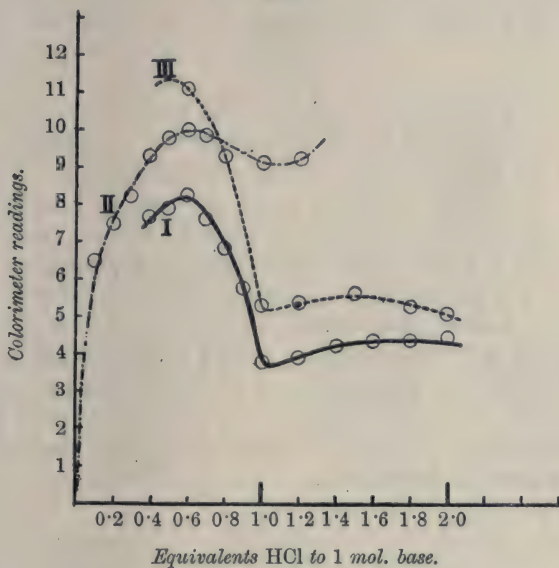
The interesting variations of colour intensity which are brought about by the gradual addition of acid to a fixed quantity of the base were studied in the following manner.

Measured quantities of a 6*N*-solution of hydrochloric acid were added to a solution of the amine, containing 1.73 grams in 30 c.c. (which formed a column about 12 cm. high when placed in one of the cylindrical tubes of a colorimeter). After each addition of acid, the colour of the resulting solution was matched by adjusting the depth

of a standard solution (generally containing 3.24 grams of the amine and 0.55 gram of hydrogen chloride in 40 c.c. of water). In the accompanying diagram, the curves show the heights of the adjustable column required to give a match with the colour produced from the fixed quantity of base by the addition of different quantities of acid.

The continuous curve (I) was obtained by using an aqueous solution and matching the colour immediately after each addition of acid, the whole series of observations occupying one to two hours. It was found, however, that the colour intensity changes on standing, and

FIG. 1.



- I. Aqueous solution—initial values.
- II. Solution in aqueous alcohol—final values.
- III. Aqueous solution—final values.

that equilibrium is only reached after two or three days. Another series of observations was therefore made with an exactly similar solution, but after each addition of acid it was kept until the colour change was complete. The dotted curve (III) gives the colour values finally attained. In neither case were the observations carried beyond the point at which 2 equivalents of acid were present, as, owing to alteration of tint, matching became difficult and uncertain. It was further observed that on the ascending limb of the curve the colour deepens with time, whilst on the descending limb it diminishes. Owing to the fact that nearly 0.4 equivalent of acid is necessary to

keep the base in solution at the ordinary temperature when water is used as solvent, readings corresponding with smaller proportions of acid could not be obtained with aqueous solutions. In order to gain some idea of the form of this part of the curve, a mixture of alcohol (1 vol.) and water (3 vols.) was used as solvent, it being then possible to obtain solutions of the above concentration with only 0.1 equivalent of acid present. The dot and dash curve (II) refers to such a solution, and gives the colour values finally attained. It is by no means continuous with curve (III), the presence of alcohol diminishing the colour intensity when the quantity of acid present falls short of that corresponding with the mono-acid salt and increasing it when the acid exceeds this amount. By using a solution of the base in absolute alcohol, much lower readings are obtained for the same amounts of acid present, although the maximum at the half equivalent is still apparent.

The most striking feature of these curves is the intensity of colour at the half equivalent of acid. This suggests that a semihydrochloride is present in the solution at this point. If this is so, then the base, although very sparingly soluble in water at 0°, should readily dissolve in a dilute solution of its monohydrochloride at that temperature. This is actually the case, more than a molecular proportion of base dissolving in a 0.11*N*-solution of its hydrochloride, as will be seen from the table below. Moreover, if a compound is formed, then the freezing point of the solution should remain approximately unaltered, since no marked change in the extent of ionisation is to be anticipated. The table shows the freezing points of a solution of 0.073 gram of hydrogen chloride in 17.3 grams of water, to which 3-aminoquinoline was added in increasing amounts:

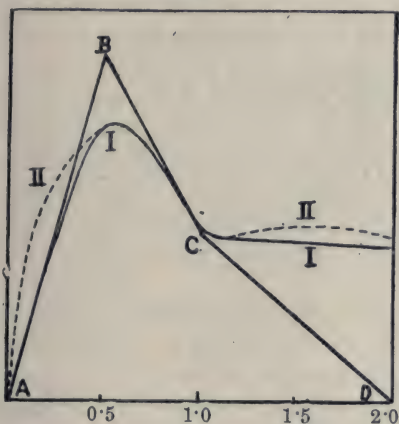
Weight (gram) of base in solution.	Equiv. of base to 1 equiv. acid.	Freezing point.
0.000	0.00	-0.437°
0.130	0.45	0.406
0.195	0.68	0.370
0.273	0.95	0.322
(Interpolated)	1.00	0.320
0.563	1.95	0.332
(Interpolated)	2.00	0.333
0.727	2.52	0.342

The depression of freezing point diminishes up to the point corresponding with the monohydrochloride, due doubtless to the smaller ionisation of this salt compared with that of hydrochloric acid. Beyond this point, although the quantities of base in solution would, if no further combination took place, produce further depressions of 0.216° and 0.337°, the actual increases in the depressions observed are only 0.010° and 0.020° respectively. The base therefore dissolves in the solution of its hydrochloride to form some compound.

This can hardly be other than the semihydrochloride, and we conclude that it is to the intensity of the colour of this salt, $(C_9H_8N_2)_2HCl$, present in the solution that the maximum of colour near 0.5 equivalent of hydrochloric acid is due.*

On the hypothesis that the base forms a deeply coloured semihydrochloride, a paler monohydrochloride, and a colourless dihydrochloride, the colour intensities of the two former being represented by *B* and *C* (Fig. 2), the colour curve would consist of the straight lines *A B C D*, provided that no dissociation of the various compounds took place. The dissociation which occurs would result in a rounding of the angles so as to produce a curve of the type (I), the first portion of which is easily shown to be a hyperbola with asymptotes parallel to

FIG. 2.



A B and *B C*. The form of the actual curve, as indicated by the dotted line (II), differs from this mainly in two respects. In the first place, the colour produced by small amounts of acid (less than 0.25 equivalent) is much greater than can be accounted for on the above hypothesis. There are, however, strong indications of the existence of more highly basic salts than the semihydrochloride; for, from the figures given in the above table of freezing points, it will be seen that it is possible to prepare a solution containing as much as $2\frac{1}{2}$ equivalents of base to 1 of acid, and that the excess of base produces no corresponding

* It should be pointed out that these effects are not confined to the hydrochloride. An experiment carried out with the sulphate gave a colour curve reproducing the main features of that of the hydrochloride, although differing somewhat in the relative values at different points of the curve. It was also found that the base dissolved in an equivalent quantity of the *N*/10-solution of the sulphate without producing any marked effect on its freezing point.

effect on the freezing point. It may therefore well be that this large initial development of colour is due to the formation of still more complex and more highly coloured salts, such as $(C_9H_8N_2)_3HCl$. The second point to be explained is the rise in colour brought about by the addition of acid to the solution of the monohydrochloride, when a diminution might rather have been expected through the production of some of the colourless dihydrochloride. However, any diminution from this cause would be slight and easily masked, since the second basic group, as is usually the case in a di-acid base, seems to be very weak, and it requires a very large excess of acid indeed to decolorise completely a solution of the hydrochloride. The deepening of the colour on this part of the curve, we believe, may be possibly referred to the effect of the excess of hydrochloric acid in repressing the ionic dissociation of the hydrochloride. Sidgwick and Tizard (Trans., 1908, 93, 194) have shown that non-ionised or half-ionised copper acetate is more deeply coloured than the copper ion. It is possible that similar relationships hold in this case, since it was found that addition of sodium chloride to the solution of the monohydrochloride of the base produced a deepening of colour similar to that brought about by the addition of acid. Thus by the addition of two molecular proportions of sodium chloride to such a solution, the colorimeter reading was raised from 5.2 to 5.7. Moreover, the less ionised sulphate is distinctly more highly coloured than the hydrochloride on this part of the curve.

It may be pointed out that the possibility of the formation of complex salts of this nature has some practical bearing on the question of the determination of the strength of organic bases by measurement of the amount of acid set free from the normal salt by hydrolytic dissociation in dilute aqueous solutions. Such methods involve the assumption that the amount of free base present is equivalent to that of the free acid. If, however, there is a possibility that an appreciable proportion of the base set free by hydrolysis may enter into combination with the ion of the normal salt, there will be a corresponding increase in the amount of free hydrochloric acid, and the hydrolytic dissociation constant calculated on the above assumption may be considerably in excess of the actual value.

3-Acetylaminquinoline.

This derivative was readily obtained by boiling the amine for five minutes with acetic anhydride. The product was then poured into water, when a white, crystalline substance soon separated. The acetyl derivative so obtained, after recrystallising from hot water, melted at 166—167°. It was soluble in dilute acids with the formation of colourless solutions:

0.1126 gave 14.15 c.c. N_2 at 14° and 770 mm. $N = 15.22$.

$C_{11}H_{10}ON_2$ requires $N = 15.06$ per cent.

Quinoline-3-azo- β -naphthol.

A solution of 3-aminoquinoline in dilute acid appeared to behave normally when treated with sodium nitrite (see 3-hydroxyquinoline, below). In order to show that a diazonium salt had been formed, the solution was added to an alkaline solution of β -naphthol. A deep red precipitate was formed, which was collected, crystallised from glacial acetic acid, and dried in a vacuum. As thus obtained, quinoline-3-azo- β -naphthol is a dark crimson powder, melting at 185 — 186° :

0.1272 gave 15.15 c.c. N_2 at 17° and 764 mm. $N = 14.18$.

$C_{19}H_{13}ON_3$ requires $N = 14.05$ per cent.

3-Hydroxyquinoline.

3-Aminoquinoline (1 mol.) was dissolved in dilute sulphuric acid (3 equiv.), cooled in ice, and to the solution was added a cold solution of sodium nitrite until the reaction was complete. No evolution of gas occurred even when kept for some time at the ordinary temperature. When the solution was warmed to about 50° , a brisk evolution of nitrogen took place, and a slightly turbid liquid was obtained. After some time, the solution deposited tufts of brown crystals of 3-hydroxyquinoline sulphate. These were purified by dissolving in hot water, boiling with a little animal charcoal, filtering, and leaving to crystallise.

The phenol itself was obtained by dissolving the sulphate in hot water, and adding a slight excess of sodium bicarbonate, when a white precipitate was formed. This was collected, dried, and crystallised from toluene or aqueous alcohol. A specimen so prepared, after drying at 120° , melted at 198° , and gave the following results on analysis:

0.1319 gave 0.3634 CO_2 and 0.0574 H_2O . $C = 75.13$; $H = 4.85$.

0.1566 „ 13.0 c.c. N_2 at 19° and 763 mm. $N = 9.80$.

C_9H_7ON requires $C = 74.48$; $H = 4.83$; $N = 9.65$ per cent.

3-Hydroxyquinoline forms colourless crystals, melting at 198° . It is nearly insoluble in cold water, but dissolves much more readily in hot water or cold alcohol. It is not very soluble in chloroform or ether, but dissolves freely in hot benzene, toluene, or xylene, from which solvents it crystallises well. The phenol is also dissolved by aqueous solutions of alkalis and acids, and exhibits faint fluorescence in the latter solutions. Aqueous solutions of 3-hydroxyquinoline or its salts give a brownish-red colour with ferric chloride.

3-Hydroxyquinoline sulphate is obtained as an intermediate product in the preparation of the phenol or by dissolving the latter in hot dilute sulphuric acid and allowing to cool, when the sparingly soluble sulphate crystallises out. Specimens obtained by both methods were analysed, with results stated below.

The sulphate is a slightly yellow, crystalline substance, containing two molecular proportions of water of crystallisation. It melts and decomposes at 190—192°, sulphur dioxide being evolved, and a yellow sublimate, melting at 186—190° (probably 3-hydroxyquinoline), being formed :

(a) 0.1454 gave 0.0800 BaSO₄. H₂SO₄ = 23.11.

(b) 0.2428 „ 0.1332 BaSO₄. H₂SO₄ = 23.04.

(C₉H₇ON)₂.H₂SO₄.2H₂O requires H₂SO₄ = 23.11 per cent.

2-Chloroquinoline-3-carboxamide.

The product of interaction of phosphoryl chloride and carbostyryl-3 carboxylic acid when added to an ice-cold and nearly saturated solution of ammonia reacts readily. After keeping for an hour and then heating, a clear solution is obtained, from which the amide separates on cooling. By recrystallising from hot water, the product may be obtained as a white solid melting at 200—201° :

0.2916 gave 0.2024 AgCl. Cl = 17.16.

C₁₀H₇ON₂Cl requires Cl = 17.17 per cent.

2-Chloro-3-aminoquinoline.

The powdered chloroamide (1 part), obtained as above described, was added to a cold solution of hypobromite (prepared by adding 1 part of bromine to 4.2 parts of potassium hydroxide in 75 parts of water). Solution took place on stirring, and the liquid was then heated to 70°. On adding acetic acid, the base separated as a precipitate, which was collected and crystallised from aqueous alcohol. About 85 per cent. of the calculated yield was obtained. The base was obtained in colourless crystals melting at 168° by recrystallising from toluene :

0.2227 gave 0.1782 AgCl. Cl = 19.77.

C₉H₇N₂Cl requires Cl = 19.86 per cent.

2-Chloro-3-aminoquinoline is readily soluble in alcohol or chloroform, less so in ether or benzene. It appears to be but feebly basic, slowly dissolving in dilute acids on warming. On adding sodium nitrite to the cold acid solution, a product is obtained which gives a crimson dye when added to an alkaline solution of β-naphthol. The amine, therefore, seems to be normally diazotised.

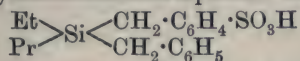
In conclusion, the authors desire to express their indebtedness to the Government Grant Committee of the Royal Society for a grant which has largely defrayed the expenses of this investigation.

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LII.—Organic Derivatives of Silicon. Part XIII. *Optically Active Compounds Containing one Asymmetric Silicon Group.*

By FREDERICK CHALLENGER and FREDERIC STANLEY KIPPING.

THE present paper contains an account of the resolution of *dl*-dibenzylethylpropylsilicanemonosulphonic acid,



(this vol., p. 149), and of the study of its optically active components. In many respects the results are of more than ordinary interest. They show, as was indeed to be expected, that a compound containing one asymmetric silicon group exists in enantiomorphously related, optically active forms. But, in addition, they prove that, even in the case of what is apparently a highly asymmetric compound, if such a term be permissible, it may be a matter of considerable difficulty to obtain any conclusive evidence of this asymmetry.

The experiments recorded in connexion with the resolution of sulphobenzylethylpropylsilicyl oxide (Kipping, *Trans.*, 1907, **91**, 209; 1908, **93**, 457) gave some indication of such difficulties. For example, only one base, out of many which were tried, accomplished the resolution of this *dl*-acid. The specific rotations of the active acids were very small (Kipping, *Trans.*, 1908, **93**, 465). Most of the salts formed by combining the active and the *dl*-acids respectively with a given active base had almost the same melting point and the same specific rotation.

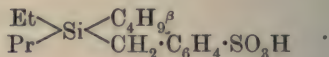
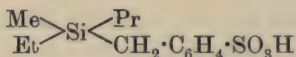
The case now to be described affords an even more striking illustration of a similar kind. Although the actual resolution of the *dl*-monosulphonic acid was accomplished with facility, as soon as, by chance, a suitable active base was discovered, it was by no means easy to prove that the acid had in fact been resolved. All the experiments made with this object led at first to negative results, that is to say, they seemed to show that the supposed

resolution products were identical with the *dl*-acid, and it was only after some time that the true nature of these products was conclusively established.

For this reason and in view of the most unusual relationship between the active and the externally compensated acids, and also because of the many possibilities of error which attend investigations of this character, the earlier part of the work is described in rather greater detail than would otherwise have been necessary.

The whole of the *dl*-acid used in these experiments had been isolated either in the form of its strychnine salt or its *l*-menthylamine salt (this vol., pp. 150, 151). As during this process these salts had been submitted to systematic fractional crystallisation, it was not impossible that the acid contained in either or both of them might be one of the optically active compounds. This, however, proved not to be the case, and so far as could be ascertained, both salts contained equal quantities of the *d*- and *l*-acids.

The *l*-menthylamine salt, as previously mentioned (*loc. cit.*), had certain characteristic properties in common with the *l*-menthylamine salts of the acids represented respectively by the following formulæ:



This fact seemed to show, not only that this salt was not a resolution product, but also that the *dl*-acid contained in it would prove to be so closely related to the two acids previously examined (Kipping, *Trans.*, 1907, **91**, 717; Kipping and Davies, *Trans.*, 1909, **95**, 69) that, like them, it would resist all attempts to resolve it.

It was therefore without any very great prospect of success that the investigation of *dl*-dibenzylethylpropylsilicanemonosulphonic acid was commenced, and the negative results which were obtained on fractionally crystallising its cinchonidine, cinchonidine hydrogen, quinine, and morphine salts only served to accentuate the probability of failure.

On preparing the brucine salt, however, there was obtained a substance which could hardly be recrystallised without its affording clear evidence of physical heterogeneity. After systematic operations, this brucine salt was easily separated into (1) a well-defined, crystalline salt, melting at 207°, which formed the most sparingly soluble component; (2) intermediate fractions of indefinite melting points; and (3) mother liquors, which, when evaporated to dryness, gave a pale yellow, vitreous product, melting at about 120–130°.

This behaviour could hardly be explained except on the

assumption that a resolution had occurred; but as some twenty salts of *dl*-acids of this type had previously been crystallised in these laboratories without any such result, the above conclusion demanded ample confirmation before it could be accepted as final.

With the object of obtaining an optically active ammonium salt, the pure, sparingly soluble brucine salt (m. p. 207°) was treated with ammonium hydroxide in aqueous-alcoholic solution; but it was impossible to get rid of the whole of the brucine. The use of sodium carbonate instead of ammonium hydroxide was equally unsuccessful; further, the liberated brucine could not be extracted from the solution with the aid of solvents.

In these circumstances the solution of the impure sodium (or ammonium) salt, prepared from the pure brucine salt, was treated with *l*-menthylamine hydrochloride, and the precipitated *l*-menthylamine salt was freed from brucine salt by fractional crystallisation from moist light petroleum.

The compound so obtained was indistinguishable in appearance from the *l*-menthylamine salt of the original *dl*-acid; it seemed to melt one degree higher than the latter, but a mixture of the two salts had practically the same melting point as either. The cinchonidine and strychnine salts prepared from the *l*-menthylamine salt of the supposed resolution product had also the same melting points respectively as the corresponding salts of the *dl*-acid.

The results obtained up to this point seemed to show, therefore, that the *dl*-acid had, in fact, been resolved, but that its optically active components underwent racemisation during the subsequent treatment of their brucine salts with alkalis.

Such an explanation could scarcely be deemed a very probable one, considering the constitution of the acid, but unless the supposed resolution products differed in composition in some unsuspected manner, it seemed to be the most reasonable one.

In order to test this possibility, samples of the two resolution products were analysed. The results agreed well in both cases with those required for a normal brucine salt of the acid; but as regards the vitreous product, they could hardly be accepted as altogether conclusive; the mode of preparation of the sample did not guarantee its purity, and the percentage composition of the normal salt was not very different from that of an acid salt, or from that of brucine acetate, either of which substances might conceivably have been present as the result of hydrolysis, or of decomposition, during the oft-repeated treatment with ethyl acetate.

Determinations of the specific rotations of the pure brucine salt (m. p. 207°) and of the vitreous product were then made, but the results were most inconclusive; the two preparations gave prac-

tically identical values, not only in methyl-alcoholic, but also in chloroform solution.

The preparation of the brucine salt was next studied quantitatively as a check on the analytical results; it was thus proved that a solution of the sodium salt, obtained from the pure *l*-menthylamine salt of the *dl*-acid, gave, with a slight excess of brucine hydrochloride, the calculated quantities of normal brucine salt, and (approximately) of sodium chloride. The brucine salt thus prepared showed the usual behaviour when it was fractionally crystallised.

In order to investigate the possibility of the occurrence of racemisation, samples of the resolution products were separately dissolved in alcohol and treated with excess of a solution of ammonium hydroxide; the solutions were then evaporated to dryness. This treatment did not change either substance, a fact which proved that the acid remained unaltered when the brucine salt was transformed into ammonium salt and back again into brucine salt.

The two resolution products were also recovered unchanged when excess of brucine hydrochloride, as well as a little ammonium hydroxide, was added to the alcoholic solutions, a fact which afforded confirmatory evidence that they were both normal salts.

The possibility that the two brucine salts might be derived from structurally isomeric acids was quite out of the question, as all the original *dl*-acid was prepared from most carefully purified material; further, the acids contained in the two brucine salts gave, when they were combined with *l*-menthylamine (or with cinchonidine or strychnine), salts which were practically indistinguishable from one another.

Now, if the above facts prove that the two brucine salts are isomeric, which they do, not only directly, but also by excluding other possibilities, they also prove conclusively that the *dl*-acid has been resolved into its enantiomorphously related components, and that the latter are not racemised by ammonium hydroxide.

The further investigation of the resolution products afforded several independent proofs of the truth of these conclusions. In the first place, it was found that when the resolution products were directly and quantitatively converted into their *l*-menthylamine salts by a simple double decomposition (p. 767), the weights of these salts corresponded exactly, within the limits of experimental error, with those which theoretically should have been obtained.

In the second place, although the *l*-menthylamine salts of the pure (*l*-) and optically impure (*d*-) acids had practically the same specific rotations as one another and as the salt of the *dl*-acid, the

melting point of the former was certainly 1° to 1.5° higher than that of the salt of the *dl*-acid; further, its solubility in light petroleum was considerably less than that of the salt of the *dl*-acid.

In the third place, it was proved that although their specific rotations were very small, the sodium salts prepared from both the resolution products were optically active in concentrated methyl-alcoholic solution. The sodium salt of the optically pure acid, prepared from the sparingly soluble brucine salt, gave a maximum value of $[\alpha]_D - 1.0^{\circ}$ approximately. The solutions of the sodium salt of the optically impure *d*-acid were dextrorotatory, and the observed rotations indicated the presence of an acid having a specific rotation of about $+1^{\circ}$.

A final and obviously a most conclusive piece of evidence was obtained in the following manner. The *l*-acid contained in the pure brucine salt was quantitatively transformed into its *l*-menthylamine salt and then into its sodium salt, and the solution of the last-named compound was precipitated with brucine hydrochloride under the usual conditions. The brucine salt thus obtained in theoretical quantity melted at 205° without even having been recrystallised. A similar series of experiments was carried out with the vitreous brucine salt (m. p. $120-130^{\circ}$), and, as far as could be ascertained from the somewhat indefinite properties of this optically impure preparation, the final product of these double decompositions was also identical with the vitreous substance from which it had been prepared.

There being no longer any question as to the nature of the resolution products, various salts of the optically pure *l*-acid were prepared by treating its sodium salt with salts of different optically active bases; the compounds thus obtained were directly compared with the corresponding salts of the *dl*-acid. Had it not been for the overwhelming nature of the evidence given above, the results of this comparison might well have cast some doubt on the relationship of the two acids; although four pairs of salts were examined, in no case was there a difference in melting point or in specific rotation well outside the limit of the possible experimental error. This will be evident from the following summary of the data obtained in the course of this comparison, including those already given in the case of the *l*-menthylamine and strychnine salts.*

* The *l*-menthylamine and strychnine salts of the *dl*-acid are described in this vol., pp. 150—152.

*Salts of dl- and l-Dibenzylethylpropylsilicanemonosulphonic Acid.**l-Menthylamine Salts.*

<i>l</i> -Acid.	<i>dl</i> -Acid.
M. p. 100·5—101·5°	M. p. 99—99·5°
$[\alpha]_D - 13·8^\circ$	$[\alpha]_D - 13·4^\circ$

Strychnine Salts.

<i>l</i> -Acid.	<i>dl</i> -Acid.
M. p. 197—198°	M. p. 197°
$[\alpha]_D - 11·1^\circ$	$[\alpha]_D - 8·3^\circ$

Cinchonidine Salts.

<i>l</i> -Acid.	<i>dl</i> -Acid.
M. p. 158—160°	M. p. 157—159°
$[\alpha]_D - 66·3^\circ$	$[\alpha]_D - 62·1^\circ$

Quinine Salts.

<i>l</i> -Acid.	<i>dl</i> -Acid.
M. p. 133—135°	M. p. 131—133°
$[\alpha]_D - 109·5^\circ$	$[\alpha]_D - 111·3^\circ$

Morphine Salts.

<i>l</i> -Acid.	<i>dl</i> -Acid.
M. p. 160—163° (turning very brown)	M. p. 155—160° (turning very brown)
$[\alpha]_D - 56·0^\circ$	$[\alpha]_D - 52·2^\circ$

Unfortunately, the salts of the *d*-acid could not be thus compared with those of the *l*- and of the *dl*-acids, as the *d*-acid has not yet been obtained in sufficient quantities in an optically pure condition; it seems probable, however, that the properties of these compounds would not differ appreciably from those of the corresponding salts of the *l*-acid.

Sufficient data are not yet available for making any general statements with respect to optically active silicon compounds, but it is certainly a striking fact that the two very different types of active acids so far examined should have such feeble rotatory powers and generally behave in other respects like symmetrical compounds.

EXPERIMENTAL.

Attempts to Resolve the dl-Acid with the aid of Cinchonidine, Quinine, and Morphine.

The *dl*-monosulphonic acid used in these earlier experiments had been isolated in the form of its strychnine salt (this vol., p. 150). From this material a solution of the ammonium salt was obtained by precipitating the alkaloid with a large excess of concentrated ammonium hydroxide in aqueous-alcoholic solution, and then

evaporating the filtered liquid. This solution, which still contained very small quantities of strychnine, was then directly used in preparing the alkaloidal salts described below, with the exception of the quinine salt, which was prepared from pure sodium salt.

The compounds were obtained by precipitation, and, after having been washed with water, were fractionally crystallised from various solvents; as there were no indications of any change having occurred, the "most sparingly soluble" fraction (A) and the "most readily soluble" fraction (B) were directly compared as regards their melting points and specific rotations, in order to try and ascertain whether a resolution had occurred or not.

In most cases a comparison of these properties would give decisive information, but in those described below, as was afterwards found, this method of examination was quite useless. Even now that the *dl*-acid has been resolved, and the salts of the *l*-acid with the alkaloids in question have been studied, it is impossible to say whether the acid was resolved or not in these earlier experiments.

Cinchonidine dl-dibenzylethylpropylsilicanemonosulphonate was crystallised from aqueous acetone about eight or ten times. The extreme fractions, which melted at the same temperature, namely, at 157—159°, were examined polarimetrically in methyl-alcoholic solution.

A. 0.6667, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 3.25^\circ$, whence $[\alpha]_D - 60.9^\circ$.

B. 0.3518, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 1.77^\circ$, whence $[\alpha]_D - 62.9^\circ$.

The salt was then crystallised seven times from dry ethyl acetate:

A. 0.5572, made up to 25 c.c., in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 2.77^\circ$, whence $[\alpha]_D - 62.1^\circ$.

An analysis of the pure salt was made in order to obtain confirmatory evidence of the nature of the acid contained in it:

0.1794 gave 0.4559 CO₂ and 0.1155 H₂O. C = 69.28; H = 7.13.

C₃₈H₄₈O₄N₂SSi requires C = 69.41; H = 7.36 per cent.

The salt is readily soluble in ethyl and methyl alcohols, chloroform, benzene, or acetone. It crystallises from hot ethyl acetate in tufts of fine prismatic needles, which are hygroscopic in presence of the solvent. In ether or light petroleum it is insoluble.

The *cinchonidine hydrogen* salt was prepared by treating the normal salt in alcoholic solution with concentrated hydrochloric acid. When dissolved in alcohol and precipitated with water, it gave an emulsion which set to a thick jelly in the course of a few moments. It was fractionally precipitated in this way eight or ten times; the fraction A decomposed at 210—211°, and the fraction B

at about 205° , but the temperature of decomposition depended on the rate of heating.

A. 0.7062, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 2.38^{\circ}$, whence $[\alpha]_D - 42.1^{\circ}$.

B. 0.6782, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 2.20^{\circ}$, whence $[\alpha]_D - 40.5^{\circ}$.

The salt was then fractionally precipitated by adding ethyl acetate to its solution in methyl alcohol; it separated in flakes devoid of definite form, and after seven operations melted at $206-210^{\circ}$:

A. 0.7583, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 2.5^{\circ}$, whence $[\alpha]_D - 41.2^{\circ}$.

The salt is readily soluble in chloroform and the common alcohols, and fairly soluble in hot benzene, toluene, or acetone, but insoluble in ether or light petroleum.

Quinine dl-dibenzylethylpropylsilicanemonosulphonate was fractionally crystallised six times from a mixture of ethyl acetate and light petroleum. The fraction A then melted at $132-133^{\circ}$, and B at $131-133^{\circ}$. The specific rotations were taken in methyl-alcoholic solution:

A. 0.4031, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 3.59^{\circ}$, whence $[\alpha]_D - 111.3^{\circ}$.

B. 0.3925, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 3.47^{\circ}$, whence $[\alpha]_D - 110.5^{\circ}$.

The salt crystallises from a mixture of ethyl acetate and light petroleum in minute clusters of radiating needles. In ethyl and methyl alcohols, acetone, benzene, toluene, chloroform, or ethyl acetate it is readily soluble, but it is insoluble in ether or light petroleum.

Morphine dl-dibenzylethylpropylsilicanemonosulphonate was fractionally crystallised from a mixture of ethyl acetate and acetone apparently without result, but the process was not continued, as, in the meantime, the brucine salt had been examined.

The morphine salt separates from the above-named mixture in very badly-defined crystals, which decompose at $155-160^{\circ}$. It is insoluble in light petroleum, ethyl acetate, or chloroform, forming a jelly with the last-named solvent. In ethyl and methyl alcohols or in acetone it is readily soluble:

0.4238, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 1.77^{\circ}$, whence $[\alpha]_D - 52.2^{\circ}$.

Resolution of dl-Dibenzylethylpropylsilicanemonosulphonic Acid.

The experiments on the resolution of *dl*-dibenzylethylpropylsilicanemonosulphonic acid with the aid of brucine have been carried out many times and with several different preparations of the acid. Most of the material which was employed had been isolated in the form of the very carefully purified *l*-menthylamine salt (this vol., p. 151), which was converted into the sodium salt by treating it with a slight excess of sodium carbonate and completely removing the liberated base by distilling it in a current of steam; the solution of the sodium salt was then concentrated and exactly neutralised with acetic acid. The actual resolution of the brucine salt is such a simple matter and is so invariably successful that it was not found necessary to study the conditions with any care; the only requisite precaution seems to be to ensure the complete precipitation of the acid in preparing its brucine salt, otherwise the precipitate seems to carry down and retain some sodium salt of the acid.

To a neutral aqueous solution of a known weight of the sodium salt an aqueous solution of brucine hydrochloride (1.1 mols.) is gradually added, the mixture being well stirred. At first the precipitate redissolves, and the liquid assumes the appearance and consistency of raw white-of-egg, but finally a viscid, colourless oil is deposited. After stirring the mixture well, the clear solution is decanted, and the oil is washed with small quantities of water until free from chloride. It is then dried in the water-oven; during this process it gradually solidifies to a brittle, vitreous mass, which, when crushed, gives a white powder. This product softens at about 145°, but does not melt completely until about 185°.

The dry salt is now heated with ethyl acetate, which may be mixed with a small proportion of acetone or a very little methyl alcohol to assist solution. As soon as the powder, or most of it, has dissolved, the solution is allowed to cool, and the crystalline deposit is collected; this first crop of crystals may melt very indefinitely at any temperature from about 160° to 190°, according to the conditions of the experiment. The first deposit is repeatedly recrystallised from ethyl acetate (which may contain a little methyl alcohol) until its melting point rises to, and remains constant at, 207°. This preparation is the brucine salt of the *l*-acid; it is only very sparingly soluble even in boiling ethyl acetate.

The mother liquors from the first deposit are left over sulphuric acid, and the subsequent crops of crystals which they afford are systematically fractionated as before from hot ethyl acetate. The salt which accumulates in the final mother liquors does not

crystallise readily, and when its solutions in ethyl acetate are evaporated over sulphuric acid, they usually afford a yellow, vitreous mass. This product is very readily soluble in cold ethyl acetate, but it separates as a crystalline powder when its solutions are very slowly evaporated in a desiccator; it is precipitated as an oil when light petroleum is added to its ethyl acetate solution, but it soon solidifies when freed from solvents.

This soluble preparation is the optically impure brucine salt of the *d*-acid; it usually melts at about 120—130°.

The final results of the fractional crystallisation of, say, 15 grams of brucine salt are approximately as follows:

I. 6 grams of optically pure salt, m. p. 207°.

II. 3 grams of intermediate fractions with indefinite melting points falling to about 140°.

III. 6 grams of optically impure salt, melting from 120—130°.

That is to say, by long-continued operations the resolution is almost complete, although the readily soluble salt of the *d*-acid cannot be obtained optically pure.

The brucine salt of the *l*-acid is readily soluble in ethyl and methyl alcohols, chloroform, or acetone, almost insoluble in hot ethyl acetate, and insoluble in light petroleum or ether; it crystallises well from aqueous alcohol or aqueous acetone, and also from a mixture of ethyl acetate and methyl alcohol.

The salt of the *d*-acid dissolves freely in the alcohols and in chloroform, acetone, or ethyl acetate, but it is insoluble in ether or light petroleum.

Attempts to Prove that a Resolution had Occurred.

When the two very different fractions of brucine salt were obtained for the first time, it only seemed necessary to decompose the pure, sparingly soluble salt with ammonia, and then to make an optical examination of the solution of the ammonium salt in order to prove that the *dl*-acid had been resolved.

Proceeding on these lines, it was found that the alkaloid was not precipitated except very partially on treating the salt with ammonium hydroxide or sodium carbonate in aqueous alcoholic solution and then evaporating the alcohol, or on boiling the salt with aqueous sodium carbonate. Further, the alkaloid could not be extracted from these alkaline solutions with solvents. Hence the polarimetric examination of the solution would have been useless.

For this reason, the impure solution of the ammonium salt was treated with *l*-menthylamine hydrochloride, and the precipitated *l*-menthylamine salt was purified by recrystallisation from light

petroleum; the product was apparently identical with the *l*-menthylamine salt of the *dl*-acid, and when mixed with the latter did not affect its melting point.

This *l*-menthylamine salt was converted into sodium salt, and from this the strychnine and cinchonidine salts were prepared; after they had been recrystallised, the melting points of these compounds were directly compared with those of the corresponding salts of the *dl*-acid. The results of this comparison seemed to prove the identity of the two acids, as will be seen from the following data:

	<i>dl</i> -Acid.	Acid from brucine salt, m. p. 207°.
<i>l</i> -Menthylamine salt.....	99—99·5°	100—101·5°
Strychnine salt	197	197—198
Cinchonidine salt	157—159	158—160

Two possibilities thus seemed to present themselves; either the acid had not been resolved, or its resolution had been accomplished, but the products had subsequently racemised.

The Resolution Products are Isomeric Normal Salts.

Assuming that the materials used in the resolution experiments were free from impurity, of which there was no doubt, and that the only insoluble product of their interaction was the normal brucine salt, it was impossible to reconcile the observed facts with the view that the acid had not been resolved.

There was, however, some uncertainty as to the second assumption, since many of the normal alkaloidal salts of sulphonic acids of silicon are readily converted into acid salts, as, for example, in the case of the cinchonidine derivative described above. Now, the readily soluble fractions of the resolved brucine salt had almost invariably an acid reaction to litmus, and, although this might be caused by slight hydrolysis, either of the salt or of the ethyl acetate used as solvent, it might conceivably be due to the presence of a brucine hydrogen salt. It was, of course, hardly possible that any large proportion of the original precipitate should consist of such an acid salt, but even a small proportion might have a considerable effect on the solubility and melting point of the normal salt. In any case analyses of the extreme fractions of the brucine salt seemed to be required, and these were carried out with the following results:

Sparingly Soluble Fraction (m. p. 207°).

0·1903 gave 0·4656 CO₂ and 0·1224 H₂O. C=66·73; H=7·14.

0·6714 „ 0·0488 SiO₂. Si=3·42.

Readily Soluble Fraction (m. p. 120—130°).

- I. 0.1580 gave 0.3850 CO₂ and 0.1032 H₂O. C=66.45; H=7.28.
 0.1618 „ 0.3938 CO₂ „ 0.1024 H₂O. C=66.37; H=7.05.
 II. 0.6722 gave 0.0532 SiO₂. Si=3.72.

I and II were different preparations.

C₄₂H₅₂O₇N₂SSi requires C=66.59; H=6.92; Si=3.66 per cent.

These results, although agreeing well with those required for the normal salt, are not, as a matter of fact, very conclusive, since an acid brucine salt containing two molecules of acid to one of alkaloid would contain C=65.4; H=6.96. The specific rotations of the two extreme fractions were then determined, both in methyl alcohol and in chloroform:

Sparingly Soluble Fraction (m. p. 207°). Dried at 100°.

3.22, in 25 c.c. chloroform, gave, in a 2-dcm. tube, α -3.05°,
 whence $[\alpha]_D$ -11.8°.

3.22, in 25 c.c. methyl alcohol, gave, in a 2-dcm. tube, α -1.59°,
 whence $[\alpha]_D$ -6.2°.

Readily Soluble Fraction (m. p. 120—130°). Dried at 100°.

3.22, in 25 c.c. chloroform, gave, in a 2-dcm. tube, α -2.73°,
 whence $[\alpha]_D$ -10.6°.

3.22, in 25 c.c. methyl alcohol, gave, in a 2-dcm. tube, α -1.37°,
 whence $[\alpha]_D$ -5.3°.

These optical data did not give any assistance in settling the nature of the salts; the fact that the two preparations had nearly the same specific rotations both in methyl-alcoholic and in chloroform solution might be taken as evidence that they were both normal salts; on the other hand, it seemed to show that they were not resolution products.

Although at this stage the facts pointed strongly in one direction, they did not prove conclusively that the extreme fractions of the brucine salt had the same composition; the following experiments were therefore made.

The preparation of the brucine salt from the *dl*-sodium salt and brucine hydrochloride was carried out quantitatively, and it was found that the calculated quantities of brucine salt and of sodium chloride were obtained; this fact showed that the precipitated brucine salt could not contain any appreciable quantity of acid salt, and yet when fractionally crystallised it behaved both qualitatively and quantitatively in the manner already described.

Samples of the extreme fractions of the resolved brucine salt were separately dissolved in alcohol and treated with excess of ammonium hydroxide, after which the solutions were evaporated to dryness; both preparations were recovered unchanged.

The two samples were also separately treated with brucine hydrochloride and a little ammonium hydroxide in alcoholic solution, and were then precipitated with water; they were both unchanged.

From these facts and the evidence already brought forward it must be concluded: (i) that the precipitated brucine salt is the pure normal salt; (ii) that it is resolved under the conditions already described; and (iii) that the active acids do not racemise when their brucine salts are treated with ammonium hydroxide.

Conversion of the Brucine Salts of the Active Acids into l-Menthylamine Salts.

Before proceeding with the study of the active acids it was necessary to devise some method of preparing, from their brucine salts, solutions of their sodium salts which would be perfectly free from brucine or other optically active impurities. This was accomplished in the following manner:

The brucine salt is mixed with excess of *l*-menthylamine hydrochloride, and, after moistening the mixture with water, it is warmed for a short time with light petroleum; the *l*-menthylamine salt of the active acid dissolves in the petroleum, which is then decanted. The extraction of the pasty mass of unchanged brucine salt, brucine hydrochloride, and *l*-menthylamine hydrochloride is continued until the residue becomes completely soluble in water and is free from the silicon compound.

The petroleum extracts are washed with two or three different concentrated aqueous solutions of *l*-menthylamine hydrochloride until the washings are free from brucine hydrochloride, and the petroleum is then evaporated; the colourless, oily *l*-menthylamine salt thus obtained is well washed with water to free it from *l*-menthylamine hydrochloride (otherwise it remains oily), and is then recrystallised from moist light petroleum.

In this way the brucine salt is quantitatively converted into the *l*-menthylamine salt, and even the coloured readily soluble resolution product gives a snow-white *l*-menthylamine salt free from all impurity except the optical isomeride.

Quantitative experiments with both the resolution products always gave results which could only have been obtained with normal brucine salts: thus, 9 grams of pure brucine salt (m. p. 207°) gave 6.3 grams of pure *l*-menthylamine salt, the quantity theoretically obtainable being 6.6 grams. The results with the readily soluble fraction were almost as good.

Comparison of the l-Menthylamine Salts of the l-, d-, and dl-Acids.

The *l*-menthylamine salt prepared from the optically pure brucine salt (m. p. 207°) was indistinguishable by inspection from the derivative of the optically impure brucine salt (m. p. 120—130°), and also from the derivative of the *dl*-acid; they all separated from moist light petroleum in hydrated, nacreous plates or prisms, which liquefied at temperatures far below 100°, and doubtless contained the same proportion of combined water. The melting points of the three preparations, dehydrated at 100° and also in a desiccator over sulphuric acid, were directly compared, and from the results of such comparisons, repeated many times, there is no doubt that the *l*-menthylamine salt of the optically pure *l*-acid melts about 1·5° higher than the salt of the *dl*-acid (m. p. 99—99·5°).

Different samples of the *l*-menthylamine salt prepared from the optically impure brucine salt always melted at temperatures below 98°, as a rule at about 96—97°, in one case, however, as low as 92—93°, but not very sharply; such specimens had often been recrystallised several times from light petroleum and were certainly chemically pure, but whether any one of them was optically pure or not cannot be stated.

A mixture of any two of the three salts had a melting point approximately the mean of those of its components.

Although so similar in the above-mentioned respects, the *l*-menthylamine salts of the active and *dl*-acids seemed to show considerable differences in solubility.

Each of the three hydrated salts (0·5 gram) was shaken with dry light petroleum (b. p. 48—62°) for about two hours, and the solutions were afterwards left for some time at the laboratory temperature (17°). They were then filtered as rapidly as possible into 25 c.c. flasks. The contents of the three flasks were finally washed out into weighed beakers, evaporated, and heated at 100° for five minutes.

The results showed that 25 c.c. of petroleum had dissolved:

0·087 of the salt of the *l*-acid.

0·118 " " " *dl*-acid.

0·112 " " " (optically impure) *d*-acid.

These values show a difference in solubility of more than 22 per cent. in the case of the salts of the *l*- and of the *dl*-acids, but they must be regarded as approximations only.

The specific rotations of the hydrated *l*-menthylamine salts prepared from the active acids were determined in methyl-alcoholic solution.

Salt of l-Acid.

3.40, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 3.52^\circ$,
whence $[\alpha]_D - 12.9^\circ$.

Calculated for anhydrous salt, $[\alpha]_D - 13.8^\circ$.

Salt of (optically impure?) d-Acid.

2.82, made up to 25 c.c., gave, in a 2-dcm. tube, $\alpha - 2.65^\circ$,
whence $[\alpha]_D - 11.7^\circ$.

Calculated for anhydrous salt, $[\alpha]_D - 12.6^\circ$.

The specific rotation of the anhydrous *l*-menthylamine salt of the *dl*-acid is -13.4° (this vol., p. 152).

The Acids are Optically Active.

Weighed quantities of the *l*-menthylamine salts prepared from the resolution products in the manner just described were converted into the sodium salts of the active acids. The aqueous solutions of these salts, which contained traces of sodium acetate (compare p. 763), were evaporated almost to dryness, and the residues were examined polarimetrically in methyl-alcoholic solution. The weight of the sodium salt contained in the solution, and given below, was calculated from that of the *l*-menthylamine salt which had been decomposed. Two different preparations of the sodium salt of the *l*-acid were examined:

I. 3.0 grams, made up to 15 c.c., gave, in a 2-dcm. tube, $\alpha - 0.25^\circ$,
whence $[\alpha]_D - 0.63^\circ$; $[M]_D - 2.4^\circ$.

II. 1.73 grams, made up to 14.3 c.c., gave, in a 2-dcm. tube,
 $\alpha - 0.21^\circ$, whence $[\alpha]_D - 0.87^\circ$; $[M]_D - 3.3^\circ$.

As the experimental error may be considerable, and as the proportion of water in the solution may have been different in the two cases, these determinations are given principally to show that the acids have a distinct rotatory power, although the specific rotation is almost certainly not greater than 1.0° .

Several concentrated solutions of the sodium salt of the optically impure *d*-acid were also examined and found to be distinctly dextro-rotatory, readings of about $\alpha + 0.1^\circ$ being obtained. As the specific rotation of the sodium salt of the acid in methyl-alcoholic solution was so very low, and as it seemed possible that higher values might be obtained with other salts of the acid in non-dissociating solvents, a few attempts were made to prepare derivatives of the desired character, but without success. None of the bases examined gave a crystalline product except β -naphthylamine, and the solutions of

this salt acquired a red tinge so rapidly that they could not be examined polarimetrically.

β-Naphthylamine 1-dibenzylethylpropylsilicanemonosulphonate crystallises from ethyl acetate in colourless needles, melting at 123—124°; it is insoluble in ether or light petroleum, but dissolves freely in benzene, chloroform, acetone, and the common alcohols.

The *β*-naphthylamine salt of the *dl*-acid was also prepared; it melted at 124—125°, and was indistinguishable in appearance from the corresponding derivative of the active acid.

Preparation of the Brucine Salts from the Active Acids.

Although no further proof of the resolution of the *dl*-acid could possibly be required, it was a matter of interest to reconvert the sodium salts of the active acids into the brucine salts. If no racemisation occurs during the various operations necessary for the preparation of the sodium salts from the resolution products, the regenerated brucine salts should be identical with the substances from which they were respectively prepared. These experiments were performed quantitatively as well as qualitatively.

The brucine salt of the *l*-acid, which was obtained in practically theoretical quantity, like the original resolution product, was almost insoluble in ethyl acetate, and without being recrystallised it melted at 205°.

The salt of the optically impure *d*-acid, likewise obtained in practically theoretical quantity, was also identical with the original resolution product from which it had been prepared, as far as could be ascertained from its ill-characterised properties.

Salts of 1-Dibenzylethylpropylsilicanemonosulphonic Acid.

The four salts about to be described were prepared by precipitating the neutral aqueous solutions of the optically pure sodium salt of the *l*-acid with the appropriate alkaloidal hydrochloride and then washing with water.

Strychnine 1-dibenzylethylpropylsilicanemonosulphonate crystallises from a mixture of ethyl acetate and acetone in beautiful, shining, prismatic needles, which resemble those of the salt of the *dl*-acid. Unless the salt has been repeatedly crystallised, these needles are hydrated and soften at 160°, drying up again, and melting finally at 197—198°, the melting point of the anhydrous salt:

0.8744 anhydrous salt, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 0.78^\circ$, whence $[\alpha]_D - 11.1^\circ$.

The salt is readily soluble in the common alcohols, chloroform,

benzene, and in hot acetone. It is very sparingly soluble in dry ethyl acetate, and is insoluble in ether or light petroleum.

Cinchonidine 1-dibenzylethylpropylsilicanemonosulphonate crystallises well from hot ethyl acetate, and cannot be distinguished from the corresponding salt of the *dl*-acid. It melts at 158—160°:

0.5280, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 2.8^\circ$, whence $[\alpha]_D - 66.3^\circ$.

This salt is readily soluble in methyl and ethyl alcohol, chloroform, and acetone, sparingly so in ethyl acetate, and insoluble in light petroleum or ether.

Quinine 1-dibenzylethylpropylsilicanemonosulphonate crystallises from a mixture of ethyl acetate and light petroleum in clusters of minute needles, which melt at 133—135°. In appearance, melting point, and specific rotation it is absolutely indistinguishable from the corresponding salt of the *dl*-acid:

0.5318, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 4.66^\circ$, whence $[\alpha]_D - 109.5^\circ$.

The quinine salt of the *l*-acid is very readily soluble in chloroform, benzene, acetone, ethyl acetate, and the common alcohols, but is insoluble in ether or light petroleum.

Morphine 1-dibenzylethylpropylsilicanemonosulphonate separates in ill-defined flakes from a mixture of acetone and ethyl acetate, and melts and decomposes at 160—163°:

0.4154, made up to 25 c.c. in methyl alcohol, gave, in a 2-dcm. tube, $\alpha - 1.86^\circ$, whence $[\alpha]_D - 56^\circ$.

Like the previous salts, it greatly resembles the corresponding salt of the externally compensated acid.

It is readily soluble in the common alcohols and in acetone, but is almost insoluble in benzene, chloroform, or ethyl acetate, and completely so in light petroleum or ether.

Attempts to Isolate an Optically Pure d-Acid.

It has already been noted (p. 764) that the quantity of the optically pure brucine salt of the *l*-acid which may be isolated when the process of resolution is carried as far as possible amounts to about 40 per cent. of the total salt employed.

As a further 20 per cent. is contained in the intermediate fractions, which are certainly mixtures, it may be concluded that the most soluble portion, representing the remaining 40 per cent., must consist to a very large extent of the brucine salt of the *d*-acid.

For the isolation of this *d*-acid in an optically pure state, the best method seemed to be to prepare from it the salt of some

optically inactive base, and then to submit this to fractional crystallisation. Assuming the *dl*-salt to be a conglomerate and not a racemic substance, this treatment should give the optically pure salt of the *d*-acid as the most sparingly soluble fraction, whilst all the salt of the *l*-acid and some of that of the *d*-acid should remain in the mother liquors.

With this object in view, the optically impure brucine salt of the *d*-acid was transformed first into the *l*-menthylamine salt and then into the sodium salt, and the solution of the last-named compound was tested with salts of many optically inactive bases. All those which were tried gave an unsatisfactory product.

The ethylamine, phenylethylamine, and pyridine salts were so readily soluble in water that they could not be obtained by precipitation, while the quinoline and tetrahydroquinoline salts, although only moderately soluble, could not be obtained in a solid state.

Under these conditions, the solution of the optically impure sodium salt was evaporated to dryness, and the residue was crystallised from moist ethyl acetate. The deposit thus obtained, which represented about one-sixth of the whole, was dextrorotatory in methyl-alcoholic solution, as was also the salt which remained in the mother liquor; the deposit was recrystallised from moist ethyl acetate, and from it the brucine and the *l*-menthylamine salts were successively prepared.

The brucine salt separated from ethyl acetate in colourless crystals, melting fairly sharply at 117—118°. The *l*-menthylamine salt melted at 97·5—98·5°, and its melting point was not changed by recrystallisation. It cannot, of course, be taken for granted that these preparations are optically pure, because of the uncertainty as to whether the *dl*-sodium salt is a conglomerate or a racemic substance, but the fairly sharp melting point of the brucine salt seems to indicate its freedom from the derivative of the *l*-acid. The high melting point of the *l*-menthylamine salt also seems to indicate optical purity, because most of the optically impure samples of the salt of the *d*-acid which have been examined melted from 95° to 97°, and some as low as 92—93°.

The Position of the Sulpho-Group in the Sulphonic Acid.

It might perhaps be deemed unnecessary to show experimentally that the sulphonic group in *dl*-dibenzylethylpropylsilicanemono-sulphonic acid is really combined with the aromatic nucleus, because the probability that it is united to a carbon atom of one of the alkyl groups is so very remote. But, inasmuch as a sulphonic

acid of the latter type might owe its optical activity to the presence of an asymmetric carbon group, the matter is of some importance.

Now, in the case of the optically active sulphonic derivative of benzylethylpropylsilicyl oxide, direct evidence bearing on this question was easily obtained; when the acid was heated with concentrated potassium hydroxide, it yielded *p*-toluenesulphonic acid (Kipping, *Trans.*, 1908, **93**, 472), a fact which proved that the sulphonic group occupied the para-position in the aromatic nucleus.

The constitution of *dl*-dibenzylethylpropylsilicanemonosulphonic acid has been established in a similar manner, but as the disulphonic acid was not of much use for other purposes, the experiments were actually made with this compound, under the assumption, which is doubtless well-founded, that the disulphonic acid is a derivative of the monosulphonic acid.

The sodium salt of the disulphonic acid was heated on the water-bath during two hours with excess of concentrated potassium hydroxide, and, after filtering from the yellow, oily decomposition product, which probably consisted of ethylpropylsilicone, the solution was neutralised with hydrochloric acid and treated with *l*-menthylamine hydrochloride. The oily precipitate, which readily solidified to a mass of needles, was collected and recrystallised once from water. It then melted at 202°, whilst a specimen of the *l*-menthylamine salt of *p*-toluenesulphonic acid melted at 203°, and a mixture of the two substances at 202–203°. The formation of *p*-toluenesulphonic acid under these conditions proves the disulphonic acid to have the constitution $\text{SiEtPr}(\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SO}_3\text{H})_2$.

Our thanks are due to the Government Grant Committee of the Royal Society for a grant in aid of this investigation.

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LIII.—*Additive Compounds of s-Trinitrobenzene with Arylamines. Combination as affected by the Constitution of the Arylamine.*

By JOHN JOSEPH SUDBOROUGH and STANLEY HOSKINGS BEARD.

In previous papers (*Trans.*, 1901, **79**, 522; 1903, **83**, 1334; 1906, **89**, 583) attention has been drawn to the readiness with which arylamines form coloured additive compounds with *s*-trinitrobenzene and other polynitro-aromatic derivatives.

The present communication deals with the relationship between the constitution of the arylamine and (a) its capacity for the formation of these additive compounds, (b) the colour of the resulting compounds. Sommerhoff (*Inaug. Diss.*, Zürich, 1904; Noelting and Sommerhoff, *Ber.*, 1906, **39**, 76) has drawn attention to the same subject.

We have worked with a number of aromatic bases of very different types, and the results we have obtained enable us to draw the following conclusions:

1. Primary arylamines, in which the amino-group is directly attached to the nucleus, form coloured additive compounds with trinitrobenzene; in the case of benzene derivatives, the stability of the compound and also the depth of colour are increased by the introduction of alkyl groups, especially in the para-position (compare aniline with *p*-toluidine and ψ -cumidine). The introduction of negative substituents does not necessarily inhibit the formation of additive compounds, since we have been able to show that *o*-, *m*-, and *p*-bromoaniline, 2:4- and 2:6-dibromoaniline, *s*-tribromoaniline, 2:3:4:6-tetrabromoaniline, 2:4-dichloro- and *s*-trichloroaniline, *o*- and *m*-nitroaniline, and *o*- and *p*-aminobenzoic acids all yield additive compounds with trinitrobenzene. It is noticeable, however, that the colours of such additive compounds are somewhat lighter than those of compounds of simple amines and trinitrobenzene, and that most of them are unstable and readily resolved into their components when crystallised from alcohol or any common solvent. It has been found that sulphanilic acid does not combine with trinitrobenzene, whereas the ethyl ester does (Sommerhoff). The position of the substituents in the amine molecule also affects the colour of the additive compound; with a para-substituent the colour is generally deeper than with a meta- or ortho-substituent (compare *m*- and *p*-bromoanilines, *o*- and *p*-aminobenzoic acids, *o*- and *p*-anisidines).

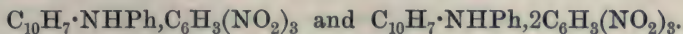
2. The primary arylamines of the naphthalene series form much more stable compounds than those of the benzene series. This applies not only to the simple amines, but to their halogen and nitro-derivatives. Thus, the compounds formed by 1-nitro-2-naphthylamine, 1:6-dibromo-2-naphthylamine, 1-bromo-2-naphthylamine, and 4-bromo-1-naphthylamine are comparatively stable. In the naphthalene, as in the benzene series, the introduction of negative substituents tends to produce lighter shades of colour.

3. Our results confirm Sommerhoff's conclusion that the presence of two or more amino-groups in the arylamine molecule tends to deepen the colour of the additive compound; thus, 1:2-, 1:4-, 1:5-, and 1:8-naphthylenediamines all form black or very deep

brown additive compounds, and triaminotoluene a stable black compound.

4. The effect of introducing alkyl or aryl radicles into the amino-group is noticeable. In the benzene or naphthalene series the tendency is for the introduction of alkyl-aryl groups to increase the depth of colour. This is well shown in the comparison of the additive compounds of β -naphthylamine with the compounds derived from its alkylated derivatives. That the effect is not always the same is shown by a comparison of the very deep red product from α -naphthylamine and trinitrobenzene with the light red product from dimethyl- α -naphthylamine and trinitrobenzene. This difference is analogous to the behaviour of the base towards Tesla rays.

All secondary amines combine with trinitrobenzene if one of the groups attached to nitrogen is an alkyl-aryl and the other an aryl. The additive compound usually contains molecular proportions of the components, but if both radicles are aryl groups the tendency is for the additive compound to contain two trinitrobenzene molecules combined with one of the base. This is shown in the following cases: diphenylamine, ditolylamine, $\beta\beta$ -dinaphthylamine, phenyl- α - and β -naphthylamine, $\alpha\alpha$ -dinaphthylamine, α -tolyl- β -naphthylamine, and p -tolyl-1-naphthylamine. That this relationship does not always hold good is shown by the fact that phenyl- β -naphthylamine forms two definite compounds, represented by the formulæ:



5. Tertiary amines also form additive compounds with trinitrobenzene, provided not more than one aryl group is attached to the nitrogen atom. Thus, additive compounds have been obtained from dimethyl- α -naphthylamine, diethyl- α -naphthylamine, dimethyl- β -naphthylamine, diethyl- β -naphthylamine, dibenzyl- β -naphthylamine, and methylethyl- α -naphthylamine.

When two aryl groups are attached to the nitrogen atom of a tertiary amine, stable additive compounds cannot always be formed. Thus, methyldiphenylamine, NMePh_2 , does not appear to yield an additive compound, but methyl- $\beta\beta$ -dinaphthylamine, $\text{NMe}(\text{C}_{10}\text{H}_7)_2$, yields a coloured product. Similarly, compounds are not formed when three aryl groups are present, as in triphenylamine.

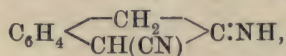
The introduction of an acetyl group into a secondary amine of the type of diphenylamine also appears to inhibit the formation of additive compounds, whereas the acetyl derivative of ethyl- β -naphthylamine forms an additive compound.

6. Sommerhoff has shown that quinoline and xyloquinoline yield colourless additive compounds with trinitrobenzene. We have con-

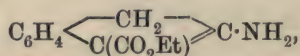
firmed these results, and also find that *iso*quinoline, *o*- and *p*-toluquinolines, and α - and β -naphthaquinolines form colourless or very pale-coloured additive compounds. The compounds contain equimolecular proportions of the base and trinitrobenzene, whereas Sommerhoff represented them as containing two of trinitrobenzene to one of base. Just as the additive compounds of trinitrobenzene with naphthylamines are more stable than those with substituted anilines (Sudborough, *Trans.*, 1901, **79**, 522), so the compounds of trinitrobenzene with naphthaquinolines are more stable than those with quinoline or alkyl-aryl-quinolines, and may be crystallised from alcohol without undergoing decomposition.

Sommerhoff states that pyridine does not form an additive compound with trinitrobenzene. We have repeated his experiment, and can confirm his conclusion, but we also find that 2:6-diphenylpyridine yields a stable additive compound, containing equimolecular proportions of base and trinitrobenzene, and crystallising from alcohol in sulphur-yellow needles. We further find that the reduction product of quinoline, namely, tetrahydroquinoline, yields a highly coloured additive compound. It thus appears that the formation of colourless or pale-coloured additive compounds is in some manner due to the double linking between carbon and nitrogen, C:N. This is supported by the fact that Schiff's bases, such as benzylideneaniline, benzylidene- α -naphthylamine, and benzylidene- β -naphthylamine, yield colourless or only very pale-coloured additive compounds with trinitrobenzene, whereas the corresponding secondary amines, benzyaniline, and benzyl- α - and benzyl- β -naphthylamines yield deeply coloured additive compounds.

We have met with one compound, containing the C:NH group, which gives a deeply coloured compound with trinitrobenzene, namely, Thorpe's β -imino- α -cyanohydrindene,



whereas a corresponding amino-compound, namely, ethyl 2-aminoindene-3-carboxylate,



yields a pale red-coloured compound.

7. Ciusa (*Gazzetta*, 1906, **36**, ii, 94) and Ciusa and Agostinelli (*Atti R. Accad. Lincei*, 1906, [v], **15**, ii, 238; 1907, [v], **16**, i, 409) have described additive compounds of phenylhydrazones with polynitro-aromatic derivatives, more especially picric acid and picryl chloride. They mention one compound with trinitrobenzene, namely, that formed by benzylidenephénylhydrazone, as crystallising in dark red needles, m. p. 134°. We have prepared similar compounds

with (1) benzylidenephénylhydrazone, (2) *m*-nitrobenzylidenephénylhydrazone, (3) cinnamylidenephénylhydrazone, (4) acetophenone-phénylhydrazone, and (5) acetonephénylhydrazone. These all form dark red crystals; 1, 3, and 4 contain two molecules of trinitrobenzene to one molecule of the hydrazone; 2 and 5 contain equimolecular proportions. The formation of such compounds was to be expected, as the hydrazones may be regarded as substituted anilines, for example, $C_6H_5 \cdot NH(N:CHPh)$.

Ciusa (*loc. cit.*) has shown that benzylideneazine, $CHPh:N \cdot N:CHPh$, forms a pale yellow additive compound with trinitrotoluene. We have been able to prepare an analogous compound with trinitrobenzene. This is of interest, as the azine contains the grouping $X \cdot CH:N$, which is also present in *iso*-quinoline (where *X* represents a benzene nucleus), and both compounds yield almost colourless additive compounds with polynitrobenzene derivatives.

8. Although aniline and its homologues yield well-defined additive compounds, aromatic amines, in which the amino-group is attached to a side-chain, and alkyl-arylamines generally yield no such compounds, although they all yield intensely deep red-coloured liquids in the presence of trinitrobenzene. Korczyński (*Bull. Acad. Sci. Cracow*, 1908, 633) describes a red additive compound, $C_6H_3(NO_2)_3 \cdot 2NH_3$, obtained by absorbing ammonia in the trinitro-derivative at -10° to -15° . In this connexion the reaction between trinitrobenzene and the reduced naphthylamines is of interest. We find that *ar*-tetrahydro- α -naphthylamine yields a well-defined, deep red, crystalline additive compound, melting at 113° , whereas the isomeric *ac*-compound produces a red coloration, but no well-defined, crystalline additive compound.

9. In a subsequent paper we shall be able to show that phenols and phenolic ethers also form definite coloured additive compounds with trinitrobenzene. It appears, therefore, all the more remarkable that when both amino- and hydroxyl groups are present in the same molecule, the compound no longer forms stable additive compounds. We have used *o*-, *m*-, and *p*-aminophenol, 2-amino- α -naphthol, and tetrabromo-*p*-hydroxydiphenylamine. If, however, the hydroxy-group is alkylated as in *o*- and *p*-anisidines and α -amino- β -naphthyl ethyl ether, coloured compounds are formed.

10. The results which we have obtained so far with heterocyclic compounds, in which the nitrogen atom forms part of the ring, do not lead to any general conclusion, but we hope to be able to extend the work in this direction. As already pointed out, quinoline and *iso*quinoline yield colourless additive compounds, whereas tetrahydroquinoline gives an almost black compound with

trinitrobenzene. The introduction of an amino-group into quinoline, as in *o*-amino-*p*-toluquinoline, leads to the formation of a red additive compound. Carbazole forms a well-defined additive compound with a bright red colour, whereas 2: 2'-diaminodiphenyl does not. Acridine yields an amber-coloured additive compound. Indole, scatole, pyrrole (Sommerhoff, *loc. cit.*), methyldole, and 1-phenyl-3-methylpyrazolone all form coloured additive compounds varying from yellow to red in colour.

The following heterocyclic compounds do not appear to yield additive compounds: 5-chloro-1-phenyl-3-methylpyrazole, 2: 4: 5-triphenylglyoxaline, amarine, pyridine, morphine, quinine, nicotine, and strychnine (von Romburgh).

11. The effects produced on the colour of the additive compound by the introduction of substituents into the primary arylamine molecule are exactly parallel to the effects produced by the same substituents on the auxochrome nature of the primary amino-group.

Kauffmann ("Die Auxochrome," *Samm. chem. tech. Vorträge*, 1907, XII, 2) draws attention to the following points:

(a) The amino-group, when directly attached to the benzene nucleus, is a powerful auxochrome.

(b) The introduction of alkyl or aryl (one) radicles into the amino-group tends to increase the auxochromic effect, as shown in the increase in depth of colour.

(c) The introduction of acyl groups tends to weaken the auxochromic nature of the amino-group.

(d) Although the introduction of two univalent alkyl groups into the amino-nucleus increases the auxochromic nature, the introduction of one bivalent group, for example, benzylidene, $C_6H_5 \cdot CH_2$, produces a considerable weakening of the auxochromic effect.

(e) The imino-group can also act as an auxochrome when it forms part of a ring-system, as in derivatives of tetrahydroquinoline, but the effect is lost when the ring contains $\cdot N \cdot$, as in quinoline derivatives. The imino-group in carbazole and hydromethylketol, and the NMe group in *N*-methyldihydromethylketol and in kairolin are auxochromes.

(f) The passage of the nitrogen atom from the ter- to the quinque-valent state destroys its auxochromic nature.

(g) The auxochrome effect is more pronounced when the hydrocarbon into which the amino-group is introduced contains two or more condensed benzene nuclei.

These broad generalisations laid down by Kauffmann hold good in the case of the additive compounds of trinitrobenzene and arylamines. Substituents which tend to increase the auxochromic

effect of the amino-group always tend to increase the depth of colour of these additive compounds, and substituents which tend to lessen or completely destroy the auxochromic nature also tend to weaken or completely remove colour from the additive compounds. Kauffmann has shown that the presence of auxochromes in aromatic compounds produces certain effects on the physical properties of the compounds. They increase the capacity for luminescence under the influence of Tesla rays, they tend to produce phosphorescence, and produce high abnormal values for both molecular magnetic rotation and molecular refraction.

The characteristic properties produced by auxochromes are due, according to Kauffmann, to a special condition of the benzene ring; the greater the effect of the auxochrome the more nearly does the benzene ring containing the auxochrome approach the D condition, a condition which is represented as analogous to the Dewar benzene formula:



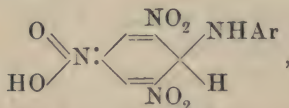
12. Molecular weight determinations of some of the additive compounds in benzene solution have shown that all those examined, namely, the compounds of trinitrobenzene with dimethyl- α -naphthylamine, tetramethyl-*p*-diaminodiphenylmethane, ethyl *p*-aminobenzoate, *p*-tolyl- α -naphthylamine, $\beta\beta$ -dinaphthylamine, ψ -cumidine, and diphenylamine, are almost completely dissociated into their components in comparatively dilute benzene solution.

13. In a few cases, where we found it difficult actually to isolate an additive compound, we have resorted to the method of determining the melting-point curve of mixtures of the components in order to make sure whether an additive compound was formed or not (compare Philip, Trans., 1903, **83**, 814; Kremann, *Monatsh.*, 1904, **25**, 1230). In the case of *o*- and *m*-nitroanilines we were able to isolate the additive compounds with trinitrobenzene by using an excess of the base and working in alcoholic solutions. With *p*-nitroaniline it was found that either one of the components or a mixture of the two separated from the alcoholic solutions. The examination of the melting-point curve proved conclusively that an additive compound is not formed. Similarly, with the nitrobenzoic acids, additive compounds were isolated from the *o*- and *p*-acids, but not with the *m*-acid. The potassium salts of all three acids, however, yield fairly stable compounds with trinitrobenzene, and also the ethyl esters of the three acids.

The melting-point curve of dinaphthyl and trinitrobenzene also shows that the two compounds form an additive compound, although

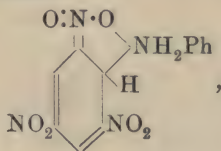
it was not found possible to isolate such a compound in the presence of solvents.

14. In one of the earlier papers (Trans., 1901, **79**, 523) various views regarding the constitution of these additive compounds have been discussed. The formation of additive compounds of trinitrobenzene and substituted pyridine and quinoline bases renders the view that the compounds have a quinonoid constitution, for example:



untenable, as the formation of such compounds in the case of quinoline would involve a rupture of the quinoline ring. The supposition that the pyridine and quinoline additive compounds have a constitution differing from that of the aniline and naphthylamine derivatives because they are much paler in colour is also improbable, since it has been shown that the introduction of negative groups into the aniline or naphthylamine molecule can lessen the depth of colour until the products have practically the same colour as certain of the compounds obtained from quinoline derivatives (compare the colour of the additive compounds from tetrabromoaniline and *o*-naphthaquinoline).

The formation of the additive compound is probably to be attributed to the latent valency of the tervalent nitrogen atom in all the amines, a conclusion which is supported by the fact that various oxygen derivatives (phenols, phenolic ethers) and sulphur compounds (thiophenols) also yield coloured additive compounds with trinitrobenzene. Whether the compounds are to be represented by a structural formula:



or not is doubtful.

EXPERIMENTAL.

I.—Additive Compounds of Trinitrobenzene with Primary Arylamines derived from Benzene or Naphthalene.

The compound with *o*-chloroaniline, $\text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Cl} \cdot \text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises from chloroform in well-developed, flat, orange-coloured prisms, or from alcohol in orange needles, melting at 134.5° : *

* The melting points are all corrected, as short normal thermometers were used throughout.

0.1778 gave 0.0734 AgCl. $\text{Cl}=10.2$.

0.250, heated at 90° , gave 0.149 $\text{C}_6\text{H}_3(\text{NO}_2)_3=59.6$.

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}_4\text{Cl}$ requires $\text{Cl}=10.4$; $\text{C}_6\text{H}_3(\text{NO}_2)_3=62.5$ per cent.

The compound with *m*-chloroaniline crystallises from alcohol in orange-coloured needles, melting at 114.5° :

0.1802 gave 0.0754 AgCl. $\text{Cl}=10.35$.

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}_4\text{Cl}$ requires $\text{Cl}=10.4$ per cent.

The compound with *p*-chloroaniline crystallises in brilliant red, prismatic needles, melting at $110-111^\circ$:

0.2027 gave 0.0840 AgCl. $\text{Cl}=10.25$.

0.7028 „ 0.4272 $\text{C}_6\text{H}_3(\text{NO}_2)_3=60.8$.*

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}_4\text{Cl}$ requires $\text{Cl}=10.4$; $\text{C}_6\text{H}_3(\text{NO}_2)_3=62.5$ per cent.

The compound with 2: 4-dichloroaniline, $\text{NH}_2\cdot\text{C}_6\text{H}_3\text{Cl}_2$, $\text{C}_6\text{H}_3(\text{NO}_2)_3$, separates from its alcoholic solution, when an excess of the base is present, in bright red needles, melting at 91° :

0.2154 gave 0.1700 AgCl. $\text{Cl}=19.5$.

$\text{C}_{12}\text{H}_8\text{O}_6\text{N}_4\text{Cl}_2$ requires $\text{Cl}=18.9$ per cent.

The compound with *s*-trichloroaniline forms yellowish-brown needles, melting at $93-94^\circ$:

0.1282 gave 0.1342 AgCl. $\text{Cl}=25.90$.

$\text{C}_{12}\text{H}_7\text{O}_6\text{N}_4\text{Cl}_3$ requires $\text{Cl}=26.01$ per cent.

The compound with *o*-bromoaniline crystallises from alcohol in orange-red needles, melting at 128° :

0.3445 gave 0.1676 AgBr. $\text{Br}=20.70$.

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}_4\text{Br}$ requires $\text{Br}=20.78$ per cent.

The compound with *m*-bromoaniline crystallises from hot alcohol in bright orange-red needles, melting at $115.5-116.5^\circ$:

0.2684 gave 0.1310 AgBr. $\text{Br}=20.77$.

0.6997 „ 0.3790 $\text{C}_6\text{H}_3(\text{NO}_2)_3=54.8$.

$\text{C}_{12}\text{H}_9\text{O}_6\text{N}_4\text{Br}$ requires $\text{Br}=20.78$; $\text{C}_6\text{H}_3(\text{NO}_2)_3=55.3$ per cent.

The compound with *p*-bromoaniline crystallises in bright scarlet needles, melting at $113-113.5^\circ$:

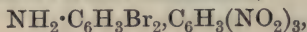
* In estimating the percentage of trinitrobenzene, the compound was usually treated with 6 c.c. of dilute hydrochloric acid until colourless, then collected, and washed with 25 c.c. of distilled water. As the trinitrobenzene is soluble in water and dilute acid, a correction was introduced. This correction was determined by treating a known weight of pure trinitrobenzene in the same manner and determining its loss in weight. For 6 c.c. of acid and 25 c.c. of water, the loss was 0.0045 gram. These aniline derivatives, unless otherwise stated, undergo decomposition when crystallised from the ordinary solvents, and can only be obtained by using solutions containing a relatively large excess of the base. Most of the naphthalene derivatives, on the other hand, can be crystallised from various solvents, including acetic acid, without using an excess of the base.

0.2820 gave 0.1368 AgBr. Br = 20.64.

0.7005 „ 0.3746 $C_6H_3(NO_2)_3$ = 54.1.

$C_{12}H_9O_6N_4Br$ requires Br = 20.78; $C_6H_3(NO_2)_3$ = 55.3 per cent.

The compound with 2: 4-dibromoaniline,



crystallises in dark orange-coloured needles, melting at 86—86.5°:

0.2048 gave 0.1656 AgBr. Br = 34.4.

$C_{12}H_8O_6N_4Br_2$ requires Br = 34.5 per cent.

The compound with 2: 6-dibromoaniline crystallises in long, canary-yellow, prismatic needles, melting at 104°:

0.4032 gave 0.3259 AgBr. Br = 34.4.

$C_{12}H_8O_6N_4Br_2$ requires Br = 34.5 per cent.

The compound with 2: 4: 6-tribromoaniline crystallises in pale orange-yellow needles, melting at 111°:

0.2024 gave 0.2117 AgBr. Br = 44.5.

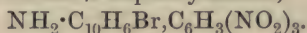
$C_{12}H_7O_6N_4Br_3$ requires Br = 44.2 per cent.

The compound with 2: 3: 4: 6-tetrabromoaniline crystallises in yellow needles, melting at 107.5—108°:

0.1896 gave 0.2310 AgBr. Br = 51.85.

$C_{12}H_6O_6N_4Br_4$ requires Br = 51.45 per cent.

Compound with α -bromo- β -naphthylamine,



—The brominated base was prepared by Morgan's method (Trans., 1900, 77, 819). The additive compound crystallises from alcohol in brilliant scarlet needles, melting at 192—192.5°:

0.1840 gave 0.0792 AgBr. Br = 18.3.

$C_{16}H_{11}O_6N_4Br$ requires Br = 18.4 per cent.

The compound crystallises well from most organic solvents, and when warmed for a few minutes with twice its weight of acetic anhydride yields the *acetyl* derivative, $NHAc \cdot C_{10}H_6Br, C_6H_3(NO_2)_3$, which crystallises in bright yellow needles, melting at 125°:

Found, N = 11.9.

$C_{18}H_{13}O_7N_4Br$ requires N = 11.75 per cent.

The same acetyl derivative is formed by the combination of *s*-trinitrobenzene and α -bromoaceto- β -naphthalide.

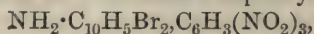
The compound with 4-bromo-1-naphthylamine crystallises in brick-red needles, melting at 195.5—196°:

0.2240 gave 0.0958 AgBr. Br = 18.2.

$C_{16}H_{11}O_6N_4Br$ requires Br = 18.4 per cent.

An acetyl derivative could not be prepared.

The compound with 1: 6-dibromo-2-naphthylamine,



crystallises from benzene or alcohol in scarlet needles, melting at 165° :

0.1500 gave 0.1093 AgBr. Br = 31.0.

$C_{16}H_{10}O_6N_4Br_2$ requires Br = 31.1 per cent.

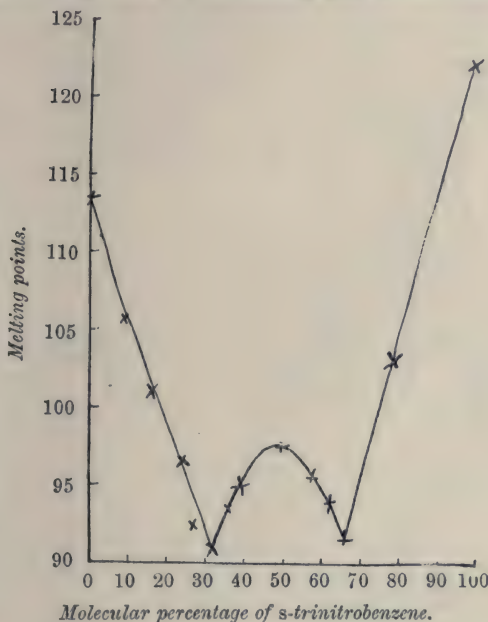
The compound with *o*-nitroaniline, $NO_2 \cdot C_6H_4 \cdot NH_2, C_6H_3(NO_2)_3$, forms brownish-yellow needles, melting at 91° :

0.4973 gave 0.2944 $C_6H_3(NO_2)_3 = 59.2$.

$C_{12}H_9O_8N_5$ requires $C_6H_3(NO_2)_3 = 60.7$ per cent.

FIG. 1.

Melting-point curve of m-nitroaniline and s-trinitrobenzene.



The compound with *m*-nitroaniline crystallises in yellow needles melting at 98° :

0.4823 gave 0.2942 $C_6H_3(NO_2)_3 = 61.0$.

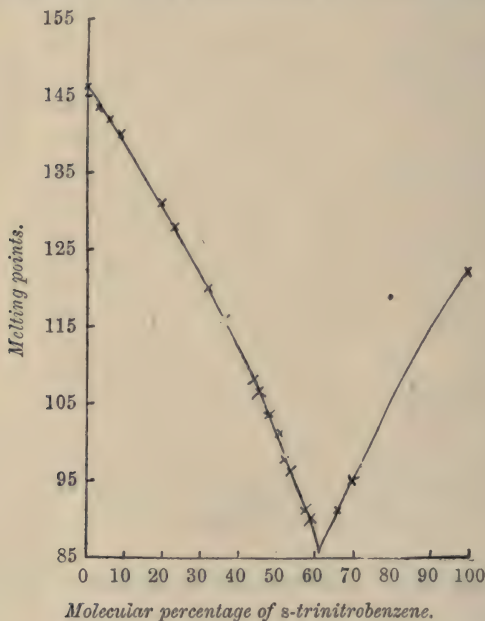
$C_{12}H_9O_8N_5$ requires $C_6H_3(NO_2)_3 = 60.7$ per cent.

The melting-point curve is given in Fig. 1.

Melting Point of Mixtures of m-Nitroaniline and s-Trinitrobenzene.

s-Trinitro- benzene, <i>m</i> -Nitroaniline, molecular percentage.	molecular percentage.	F. p.	s-Trinitro- benzene, <i>m</i> -Nitroaniline, molecular percentage.	molecular percentage.	F. p.
100.0	0.0	122.0°	39.3	60.7	95.0°
79.0	21.0	103.0	39.0	61.0	95.0
66.3	33.7	91.5	35.8	64.2	93.5
61.7	38.3	94.0	31.8	68.2	91.0
57.5	42.5	95.6	27.3	72.7	92.7
54.3	45.7	96.0	22.2	77.8	96.7
51.5	48.5	96.5	15.9	84.1	101.2
49.5	50.5	97.5	9.1	90.9	105.7
44.0	56.0	95.5	0.0	100.0	113.5

FIG. 2.

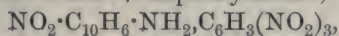
Melting-point curve of p-nitroaniline and s-trinitrobenzene.

p-Nitroaniline and trinitrobenzene do not form an additive compound, as is shown by the melting-point curve (Fig. 2). The following table gives the data for the curve:

Melting-point Curve of p-Nitroaniline and s-Trinitrobenzene.

<i>s</i> -Trinitro- benzene, molecular percentage.	<i>p</i> -Nitro- aniline, molecular percentage.	F. p.	<i>s</i> -Trinitro- benzene, molecular percentage.	<i>p</i> -Nitro- aniline, molecular percentage.	F. p.
100·0	0·0	121·7°	47·3	52·7	104·0°
69·8	30·2	94·8	45·7	54·3	106·6
65·9	34·1	90·9	44·8	55·2	106·6
62·3	37·7	89·7	43·8	56·2	108·0
59·1	40·9	90·5	42·4	57·6	108·7
57·6	42·4	90·8	40·4	59·6	110·9
55·5	44·5	92·7	36·6	63·4	115·7
53·7	46·3	95·7	32·0	68·0	119·9
52·0	48·0	97·5	23·0	77·0	128·0
50·5	49·5	100·8	19·6	80·4	130·9
50·0	50·0	101·0	8·8	91·2	139·8
49·8	50·2	100·2	6·2	93·8	142·2
49·3	50·7	102·0	3·2	96·8	143·6
48·2	51·8	103·4	0·0	100·0	146·2

The compound with α -nitro- β -naphthylamine,



crystallises from alcohol in golden-yellow needles, melting at 115·5—116°:

0·1500 gave 22·4 c.c. N_2 (moist) at 15° and 760 mm. $\text{N}=17·49$.

$\text{C}_{16}\text{H}_{11}\text{O}_8\text{N}_5$ requires $\text{N}=17·45$ per cent.

The compound is fairly stable, and can be crystallised from chloroform, benzene, ether, or carbon disulphide.

The compound with *o*-anisidine, $\text{OMe} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises from hot alcohol in glistening, brownish-red plates, melting at 98°:

0·1468 gave 21·0 c.c. N_2 (moist) at 12° and 762 mm. $\text{N}=17·0$.

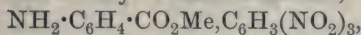
$\text{C}_{13}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{N}=16·7$ per cent.

The compound with *p*-anisidine crystallises in well-developed, lustrous, black prisms or plates, melting at 81—82°:

0·1481 gave 21·2 c.c. N_2 (moist) at 11° and 764 mm. $\text{N}=17·16$.

$\text{C}_{13}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{N}=16·7$ per cent.

The compound with methyl *o*-aminobenzoate,



crystallises from alcohol in orange-yellow needles, melting at 106°:

0·5989 gave 0·3417 $\text{C}_6\text{H}_3(\text{NO}_2)_3=57·8$.

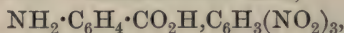
$\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3=58·5$ per cent.

The corresponding *ethyl* derivative, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Et}, \text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises in bright red needles, melting at 71—71·5°:

0·8634 gave 0·5080 $\text{C}_6\text{H}_3(\text{NO}_2)_3=58·8$.

$\text{C}_{15}\text{H}_{14}\text{O}_8\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3=56·4$ per cent.

The *compound* with *o*-aminobenzoic acid,

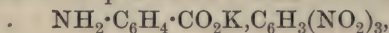


crystallises in orange-yellow needles, melting at 192—193°:

0.5 gave 0.2952 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 59.9$.

$\text{C}_{13}\text{H}_{10}\text{O}_8\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 60.8$ per cent.

The *compound* with potassium *o*-aminobenzoate,

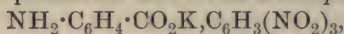


crystallises in deep red needles, melting at 114°:

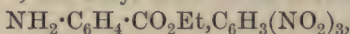
1.0 gave 0.5064 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 51.1$.

$\text{C}_{13}\text{H}_9\text{O}_8\text{N}_4\text{K}$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 54.9$ per cent.

m-Aminobenzoic acid and trinitrobenzene do not form an additive compound, but the potassium salt forms a *compound*,

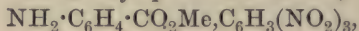


crystallising in dark reddish-brown, glistening needles, and melting at about 118—119°; the ethyl ester forms a *compound*,



melting at 84—85°.

The *compound* with methyl *p*-aminobenzoate,



crystallises in deep orange-coloured needles, melting at 114—114.5°:

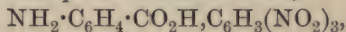
0.2050 gave 27.0 c.c. N_2 (moist) at 11° and 759 mm. $\text{N} = 15.7$.

0.6864 „ 0.3947 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 58.1$.

$\text{C}_{14}\text{H}_{12}\text{O}_8\text{N}_4$ requires $\text{N} = 15.4$; $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 58.5$ per cent.

The corresponding *ethyl* derivative crystallises from benzene in bright scarlet needles, melting at 85°.

The *compound* with *p*-aminobenzoic acid,



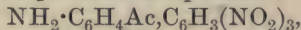
forms red, glistening crystals, melting at 151°:

0.7069 gave 0.4100 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 58.4$.

$\text{C}_{13}\text{H}_{10}\text{O}_8\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 60.8$ per cent.

The corresponding *potassium* salt forms dark red needles, which decompose at 111°.

The *compound* with *p*-aminoacetophenone,

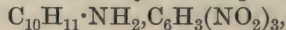


crystallises from alcohol in brilliant scarlet, flat prisms, melting at 137.3°:

0.5168 gave 0.3066 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 60.2$.

$\text{C}_{14}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 61.2$ per cent.

The *compound* with *ar*-tetrahydro- α -naphthylamine,



crystallises from hot alcohol in brick-red needles, melting at 113°:

0.5164 gave 0.3048 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 59.1$.

$\text{C}_{16}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 59.2$ per cent.

The compound with triaminotoluene, $C_6H_2Me(NH_2)_3, C_6H_3(NO_2)_3$, crystallises from alcohol in deep greenish-black needles, which decompose at 159.5° :

0.4685 gave 0.2734 $C_6H_3(NO_2)_3 = 59.3$.

$C_{13}H_{14}O_6N_6$ requires $C_6H_3(NO_2)_3 = 60.8$ per cent.

The compound with 2:4-diaminoazobenzene,



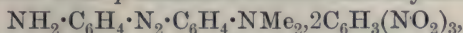
crystallises from alcohol or chloroform in glistening, black prisms, with a high metallic lustre, melting at 144° :

0.2 gave 38.6 c.c. N_2 at 10° and 758 mm. $N = 23.05$.

$C_{18}H_{15}O_6N_7$ requires $N = 23.06$ per cent.

The isomeric 3:3-diamino-compound crystallises in dark reddish-brown needles, melting at 188° , after sintering at 184° .

The compound with *p*-aminobenzeneazodimethylaniline,



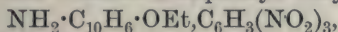
crystallises from alcohol in deep brown plates, melting at $157-158^\circ$:

0.1497 gave 26.1 c.c. N_2 at 12° and 762 mm. $N = 20.75$.

0.5008 „ 0.3198 $C_6H_3(NO_2)_3 = 64.7$.

$C_{26}H_{22}O_{12}N_{10}$ requires $N = 21.0$; $C_6H_3(NO_2)_3 = 64.0$ per cent.

The compound with α -amino- β -naphthyl ethyl ether,

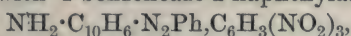


crystallises from alcohol in silky needles of a deep purple-black colour, melting at 148° :

0.1847 gave 21.6 c.c. N_2 at 9° and 757 mm. $N = 14$.

$C_{18}H_{16}O_7N_4$ requires $N = 14.0$ per cent.

The compound with 1-benzeneazo-2-naphthylamine,

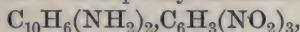


crystallises in dark red, feathery needles, melting at 153° :

0.2028 gave 31.3 c.c. N_2 at 13° and 760 mm. $N = 18.24$.

$C_{22}H_{16}O_6N_6$ requires $N = 18.26$ per cent.

The compound with 1:2-naphthylenediamine,



crystallises from alcohol or benzene in deep purple-coloured needles, melting at $203-204^\circ$. It was analysed by passing dry hydrogen chloride into the benzene solution and removing the precipitated diamine hydrochloride:

0.3460 gave 0.1938 $C_6H_3(NO_2)_3 = 56$ and 0.1519 $C_{10}H_6(NH_2)_2 = 43.9$.

$C_{16}H_{13}O_6N_5$ requires $C_6H_3(NO_2)_3 = 57.4$; $C_{10}H_6(NH_2)_2 = 42.6$ per cent.

The compound with 1:4-naphthylenediamine crystallises from

benzene or toluene in glistening, black needles, melting and decomposing at 218° :

0.500 gave 0.3006 $C_6H_3(NO_2)_3 = 60.1$.

$C_{16}H_{13}O_6N_5$ requires $C_6H_3(NO_2)_3 = 57.4$ per cent.

The isomeric 1: 5-diamine combines with trinitrobenzene, yielding a *compound*, which crystallises from alcohol in deep brown needles, melting at 245° :

0.5 gave 0.283 $C_6H_3(NO_2)_3 = 56.6$.

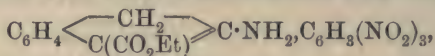
$C_{16}H_{13}O_6N_5$ requires $C_6H_3(NO_2)_3 = 57.4$ per cent.

The 1: 8-diamine yields a *compound*, which crystallises from alcohol in slender, dark brown needles, melting at 225° :

0.5 gave 0.2795 $C_6H_3(NO_2)_3 = 55.9$.

$C_{16}H_{13}O_6N_5$ requires $C_6H_3(NO_2)_3 = 57.4$ per cent.

The *compound* with ethyl 2-aminoindene-3-carboxylate,



crystallises from alcohol in small, orange-red plates, melting at 132.5° :

0.1478 gave 16.4 c.c. N_2 at 14° and 756 mm. $N = 13.0$.

$C_{18}H_{16}O_8N_4$ requires $N = 13.5$ per cent.

II.—Additive Compounds of Trinitrobenzene with Secondary Amines derived from Benzene or Naphthalene.

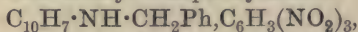
The *compound* with benzyllaniline, $NHPh \cdot CH_2Ph, C_6H_3(NO_2)_3$ crystallises from alcohol in deep red, glistening, hexagonal plates, melting at 92° :

0.1639 gave 19.6 c.c. N_2 at 13° and 758 mm. $N = 14.08$.

$C_{19}H_{16}O_6N_4$ requires $N = 14.14$ per cent.

Allylaniline also yields a coloured *compound*, but this is unstable, and becomes colourless when exposed to the air.

The *compound* with benzyl- α -naphthylamine,



crystallises from benzene in slender, chocolate-red needles, melting at $174-174.5^{\circ}$:

0.200 gave 21.5 c.c. N_2 (moist) at 14° and 765 mm. $N = 12.73$.

$C_{23}H_{18}O_6N_4$ requires $N = 12.56$ per cent.

The *compound* with benzyl- β -naphthylamine crystallises from alcohol in dark reddish-brown needles, melting at 141° . It also crystallises well from benzene or glacial acetic acid:

0.300 gave 32.5 c.c. N_2 (moist) at 11° and 738 mm. $N = 12.5$.

$C_{23}H_{18}O_6N_4$ requires $N = 12.56$ per cent.

The *compound* of benzyl- β -naphthylamine and trinitrotoluene,

$C_{10}H_7 \cdot NH \cdot CH_2Ph, C_6H_2Me(NO_2)_3$, crystallises from alcohol in brilliant, crimson needles, melting at 106.5° :

0.300 gave 29.9 c.c. N_2 (moist) at 12° and 781 mm. $N=12.2$.

$C_{24}H_{20}O_6N_4$ requires $N=12.2$ per cent.

The compound of phenyl- α -naphthylamine and trinitrobenzene, $NHPh \cdot C_{10}H_7, 2C_6H_3(NO_2)_3$, crystallises in deep purple-coloured needles, or from chloroform in glistening, deep brown prisms, melting at 130° :

0.2000 gave 25.2 c.c. N_2 (moist) at 10° and 770 mm. $N=15.3$.

2.067 „ 1.380 $C_6H_3(NO_2)_3=66.7$.*

$C_{28}H_{19}O_{12}N_7$ requires $N=15.2$; $C_6H_3(NO_2)_3=66.0$ per cent.

An acetyl derivative of the compound could not be prepared.

The compound of phenyl- β -naphthylamine and trinitrobenzene, $NHPh \cdot C_{10}H_7, 2C_6H_3(NO_2)_3$, crystallises from alcohol in deep reddish-brown plates, melting at 115.5° :

0.2017 gave 25.2 c.c. N_2 (moist) at 9° and 770 mm. $N=15.2$.

0.8043 „ 0.5228 $C_6H_3(NO_2)_3=65.0$.

$C_{28}H_{19}O_{12}N_7$ requires $N=15.2$; $C_6H_3(NO_2)_3=66.0$ per cent.

Phenyl- β -naphthylamine and trinitrobenzene also form an additive compound containing equimolecular proportions of the constituents. It crystallises from alcohol in brick-red needles, melting at 109° :

0.3050 gave 33.7 c.c. N_2 at 12° and 763 mm. $N=13.16$.

$C_{22}H_{16}O_6N_4$ requires $N=12.96$ per cent.

An acetyl derivative was obtained by warming the additive compound with twice its weight of acetic anhydride for 1.5 hours. It crystallises from alcohol in olive-green coloured needles, melting at $96-97^\circ$:

0.3016 gave 30 c.c. N_2 (moist) at 12° and 776 mm. $N=12.1$.

$C_{24}H_{18}O_7N_4$ requires $N=11.9$ per cent.

The compound of phenyl- α -naphthylamine and trinitrotoluene, $NHPh \cdot C_{10}H_7, 2C_6H_2Me(NO_2)_3$, crystallises from alcohol in dark red needles, melting at $73-74^\circ$:

0.3016 gave 37.4 c.c. N_2 (moist) at 11° and 762 mm. $N=14.83$.

$C_{30}H_{23}O_{12}N_7$ requires $N=14.56$ per cent.

The compound of $\alpha\alpha$ -dinaphthylamine and trinitrobenzene, $NH(C_{10}H_7)_2, 2C_6H_3(NO_2)_3$, crystallises from chloroform in brown, prismatic plates, melting at $156-157^\circ$:

* The trinitrobenzene was estimated by dissolving the additive compound in warm benzene, passing in dry hydrogen chloride until the colour of the solution was removed, filtering, washing, and evaporating the filtrate and washings to dryness,

0.2122 gave 26.3 c.c. N_2 (moist) at 16° and 760 mm. $N=14.45$.

$C_{32}H_{21}O_{12}N_7$ requires $N=14.1$ per cent.

The compound of $\beta\beta$ -dinaphthylamine and trinitrobenzene, $NH(C_{10}H_7)_2 \cdot 2C_6H_3(NO_2)_3$, crystallises from toluene in deep prune-brown prisms, melting at 174° :

0.1948 gave 23 c.c. N_2 (moist) at 14° and 745 mm. $N=13.6$.

$C_{32}H_{21}O_{12}N_7$ requires $N=14.1$ per cent.

The compound of *o*-tolyl- β -naphthylamine and trinitrobenzene, $C_7H_7 \cdot NH \cdot C_{10}H_7 \cdot 2C_6H_3(NO_2)_3$, crystallises from alcohol in deep crimson-red, lustrous plates, melting at 120.5 — 121° :

0.1608 gave 21 c.c. N_2 (moist) at 14° and 747 mm. $N=15.1$.

$C_{29}H_{21}O_{12}N_7$ requires $N=14.9$ per cent.

The compound of *p*-tolyl- α -naphthylamine and trinitrobenzene, $C_7H_7 \cdot NH \cdot C_{10}H_7 \cdot 2C_6H_3(NO_2)_3$, crystallises from alcohol in dark brown plates, melting at 124° :

0.1494 gave 19.1 c.c. N_2 (moist) at 12° and 762 mm. $N=15.2$.

$C_{29}H_{21}O_{12}N_7$ requires $N=14.9$ per cent.

The compound of *p*-tolyl- β -naphthylamine and trinitrobenzene, $C_7H_7 \cdot NH \cdot C_{10}H_7 \cdot 2C_6H_3(NO_2)_3$, crystallises from alcohol in bright brick-red plates, melting at 111 — 111.5° :

0.2022 gave 25.7 c.c. N_2 (moist) at 13° and 752 mm. $N=14.9$.

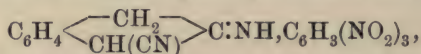
$C_{29}H_{21}O_{12}N_7$ requires $N=14.9$ per cent.

The compound of ethyl β -anilinocrotonate and trinitrobenzene, $CH_3 \cdot C(NHPh) \cdot CH \cdot CO_2Et \cdot C_6H_3(NO_2)_3$, crystallises in bright scarlet, flat prisms, melting at 126° :

0.5966 gave 0.4057 $C_6H_3(NO_2)_3 = 68.7$.

$C_{18}H_{18}O_8N_4$ requires $C_6H_3(NO_2)_3 = 67.5$ per cent.

The compound of β -imino- α -cyanohydrindene and trinitrobenzene,



crystallises from alcohol in glistening, deep black plates, melting at 168 — 169° :

0.1522 gave 24.8 c.c. N_2 (moist) at 16° and 763 mm. $N=19.1$.

$C_{16}H_{11}O_6N_5$ requires $N=19.0$ per cent.

The compound of formo- α -naphthalide and trinitrobenzene, $C_{10}H_7 \cdot NH \cdot CO \cdot H \cdot C_6H_3(NO_2)_3$, crystallises from alcohol or chloroform in yellow, felted needles, melting at 160° :

0.2014 gave 25.3 c.c. N_2 (moist) at 9° and 740 mm. $N=14.7$.

$C_{17}H_{12}O_7N_4$ requires $N=14.6$ per cent.

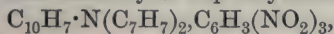
The isomeric β -compound forms yellow needles, melting at 123° :

0.2068 gave 25.8 c.c. N_2 (moist) at 14° and 762 mm. $N=14.7$.

$C_{17}H_{12}O_7N_4$ requires $N=14.6$ per cent.

III.—*Additive Compounds of Trinitrobenzene with Tertiary Amines derived from Benzene or Naphthalene.*

The compound with dibenzyl- β -naphthylamine,

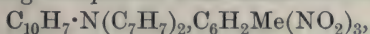


crystallises from benzene or alcohol in deep purple-black needles, melting at $126\text{--}126\cdot5^\circ$:

0.300 gave $27\cdot3$ c.c. N_2 (moist) at $13\cdot5^\circ$ and 752 mm. $\text{N}=10\cdot6$.

$\text{C}_{30}\text{H}_{24}\text{O}_6\text{N}_4$ requires $\text{N}=10\cdot5$ per cent.

The corresponding compound with trinitrotoluene,

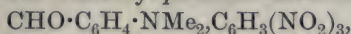


crystallises from alcohol in glistening, deep brick-red needles, melting at 108° :

Found, $\text{N}=10\cdot1$.

$\text{C}_{31}\text{H}_{26}\text{O}_6\text{N}_4$ requires $\text{N}=10\cdot2$ per cent.

The compound with dimethyl-*p*-aminobenzaldehyde,



crystallises from alcohol in deep purplish-brown, glistening needles, melting at 91° :

0.6015 gave $0\cdot3429$ $\text{C}_6\text{H}_3(\text{NO}_2)_3=57\cdot8$.

$\text{C}_{15}\text{H}_{14}\text{O}_7\text{N}_4$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3=58\cdot8$ per cent.

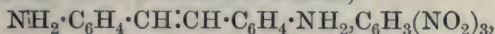
The compound with diethylaminobenzylidene-*p*-aminomethylaniline, $\text{NEt}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NHMe}$, $\text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises from alcohol in glistening, black plates, melting at $162\cdot5^\circ$:

0.1533 gave $23\cdot7$ c.c. N_2 (moist) at 15° and 747 mm. $\text{N}=17\cdot8$.

$\text{C}_{24}\text{H}_{25}\text{O}_6\text{N}_6$ requires $\text{N}=17\cdot0$ per cent.

IV.—*Additive Compounds of Trinitrobenzene with Amines derived from Di- and Tri-phenylmethane, Dibenzyl, etc.*

The compound with *oo*-diaminostilbene,

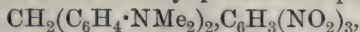


crystallises from alcohol in deep purple-brown needles, melting at $190\text{--}191^\circ$:

0.1572 gave $23\cdot6$ c.c. N_2 (moist) at 13° and 762 mm. $\text{N}=17\cdot8$.

$\text{C}_{20}\text{H}_{17}\text{O}_6\text{N}_5$ requires $\text{N}=17\cdot6$ per cent.

The compound with tetramethyl-*p*-diaminodiphenylmethane,



crystallises from alcohol in black, glistening needles, melting at $114\text{--}114\cdot5^\circ$:

0.6021 gave $0\cdot2710$ $\text{C}_6\text{H}_3(\text{NO}_2)_3=45\cdot75$.

$\text{C}_{23}\text{H}_{25}\text{O}_6\text{N}_5$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3=45\cdot6$ per cent.

The *compound* with tetramethyldiaminobenzhydrol,
 $\text{OH}\cdot\text{CH}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$,
 also crystallises in black, glistening needles, melting at $75\cdot5^\circ$:
 $0\cdot200$ gave 25 c.c. N_2 (moist) at 15° and 770 mm. $\text{N}=14\cdot8$.
 $\text{C}_{23}\text{H}_{25}\text{O}_7\text{N}_5$ requires $\text{N}=14\cdot5$ per cent.

The *compound* with tetramethyldiaminobenzophenone,
 $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in dark red plates, melting at 123° :
 $0\cdot2028$ gave $25\cdot3$ c.c. N_2 (moist) at 14° and 756 mm. $\text{N}=14\cdot6$.
 $\text{C}_{23}\text{H}_{23}\text{O}_7\text{N}_5$ requires $\text{N}=14\cdot56$ per cent.

The *compound* with tetramethyldiaminobenzophenone,
 $\text{CO}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in bright red needles, darkens at 100 — 101° ,
 and melts at 105° :

$0\cdot1911$ gave $26\cdot7$ c.c. N_2 at 14° and 756 mm. $\text{N}=16\cdot35$.
 $\text{C}_{29}\text{H}_{26}\text{O}_{13}\text{N}_8$ requires $\text{N}=16\cdot15$ per cent.

The *compound* with tetramethyldiaminothiobenzophenone,
 $\text{CS}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in long, black needles, with a green,
 metallic lustre, melting at 184 — 185° :

$0\cdot4329$ gave $0\cdot2034$ BaSO_4 . $\text{S}=6\cdot44$.
 $\text{C}_{23}\text{H}_{23}\text{O}_6\text{N}_5\text{S}$ requires $\text{S}=6\cdot44$ per cent.

The *compound* with tetramethyldiaminotriphenylmethane,
 $\text{CHPh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in black, glistening plates, melting at
 $88\cdot5$ — 89° :

$0\cdot2035$ gave 22 c.c. N_2 (moist) at 12° and 770 mm. $\text{N}=13\cdot0$.

$0\cdot5989$ „ $0\cdot2219$ $\text{C}_6\text{H}_3(\text{NO}_2)_3=37\cdot8$.

$\text{C}_{29}\text{H}_{29}\text{O}_6\text{N}_5$ requires $\text{N}=12\cdot9$; $\text{C}_6\text{H}_3(\text{NO}_2)_3=39\cdot2$ per cent.

The *compound* with tetramethyl-*p*-phenylenediamine,
 $\text{C}_6\text{H}_4(\text{NMe}_2)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in deep black, glistening needles, melting
 at 142° :

$0\cdot1569$ gave 25 c.c. N_2 at $15\cdot5^\circ$ and 758 mm. $\text{N}=18\cdot6$.

$\text{C}_{16}\text{H}_{19}\text{O}_6\text{N}_5$ requires $\text{N}=18\cdot6$ per cent.

Solutions of the compound in most solvents have a deep indigo-blue colour, and its solution in carbon disulphide a bay-green colour, whereas most of the other additive compounds give orange, red, brown, or purple coloured solutions.

V.—*Additive Compounds of Trinitrobenzene with Schiff's Bases.*

The compound with benzylideneaniline, $\text{CHPh:NPh}, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$, crystallises from alcohol in glistening, yellow, hexagonal plates, melting at 112° :

0.1521 gave 20.6 c.c. N_2 (moist) at 13° and 760 mm. $\text{N} = 16.0$.

$\text{C}_{25}\text{H}_{17}\text{O}_{12}\text{N}_7$ requires $\text{N} = 16.1$ per cent.

The compound with benzylidene- α -naphthylamine,
 $\text{CHPh:N}\cdot\text{C}_{10}\text{H}_7, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises in brownish-yellow needles, melting at 104° :

0.1584 gave 17.2 c.c. N_2 (moist) at 14° and 756 mm. $\text{N} = 12.7$.

$\text{C}_{23}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{N} = 12.6$ per cent.

The compound with benzylidene- β -naphthylamine,
 $\text{CHPh:N}\cdot\text{C}_{10}\text{H}_7, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises in deep yellow-coloured needles, melting at 150.5 — 151° :

0.2057 gave 25.6 c.c. N_2 (moist) at 10° and 768 mm. $\text{N} = 15.05$.

$\text{C}_{29}\text{H}_{19}\text{O}_{12}\text{N}_7$ requires $\text{N} = 14.9$ per cent.

VI.—*Additive Compounds of Trinitrobenzene with Phenylhydrazones.*

The compound with benzaldehydephenylhydrazone,
 $\text{CHPh:N}\cdot\text{NHPh}, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in very dark red, glistening needles, melting at 134° :

0.1470 gave 22.2 c.c. N_2 (moist) at 12° and 764 mm. $\text{N} = 18.02$.

$\text{C}_{25}\text{H}_{18}\text{O}_{12}\text{N}_8$ requires $\text{N} = 18.01$ per cent.

The compound with *m*-nitrobenzaldehydephenylhydrazone,
 $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH:N}\cdot\text{NHPh}, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in deep brick-red, slender needles, melting at 134.5° :

0.8157 gave 0.3997 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 49.0$.

$\text{C}_{19}\text{H}_{14}\text{O}_8\text{N}_6$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 47$ per cent.

The compound with cinnamaldehydephenylhydrazone,
 $\text{CHPh:CH}\cdot\text{CH:N}\cdot\text{NHPh}, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises from alcohol in deep brownish-red, glistening plates, melting at 164.5° :

0.1550 gave 22.4 c.c. N_2 (moist) at 12° and 764 mm. $\text{N} = 17.24$.

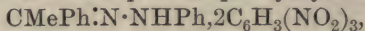
$\text{C}_{27}\text{H}_{20}\text{O}_{12}\text{N}_8$ requires $\text{N} = 17.28$ per cent.

The compound with acetonephenylhydrazone,
 $\text{CMe}_2\cdot\text{N}\cdot\text{NHPh}, 2\text{C}_6\text{H}_3(\text{NO}_2)_3$,
 crystallises in reddish-brown needles, melting at 86.5 — 87° :

0.5658 gave 0.3303 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 58.4$.

$\text{C}_{15}\text{H}_{15}\text{O}_6\text{N}_5$ requires $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 59$ per cent.

The compound with acetophenonephenylhydrazone,



crystallises in dark red needles, melting at 113.5° :

0.1528 gave 23 c.c. N_2 (moist) at 13.5° and 764 mm. $\text{N} = 17.8$.

$\text{C}_{26}\text{H}_{20}\text{O}_{12}\text{N}_8$ requires $\text{N} = 17.6$ per cent.

VII.—Additive Compounds of Trinitrobenzene with Cyclic Amines containing a Nitrogen Atom as part of the Ring.

Compound with $\alpha\alpha$ -diphenylpyridine, $\text{C}_5\text{NH}_3(\text{C}_6\text{H}_5)_2, \text{C}_6\text{H}_3(\text{NO}_2)_3$.—Although pyridine itself does not yield an additive compound with trinitrobenzene (Sommerhoff, *Inaug. Diss.*, p. 89; van Romburgh, *Rec. trav. chim.*, 1895, **14**, 67), its diphenyl derivative yields a stable additive compound, which crystallises from a hot alcoholic solution containing equivalent quantities of the base and trinitrobenzene. It forms lemon-yellow needles, melting at 113° :

0.2010 gave 21.8 c.c. N_2 (moist) at 14° and 757 mm. $\text{N} = 12.7$.

$\text{C}_{23}\text{H}_{16}\text{O}_6\text{N}_4$ requires $\text{N} = 12.6$ per cent.

The compound with $\gamma\gamma$ -dipyridyl, $\text{C}_5\text{NH}_4\cdot\text{C}_5\text{NH}_4, \text{C}_6\text{H}_3(\text{NO}_2)_3$, cannot be prepared by crystallising a mixture of the two components from a solvent, but that such a compound exists has been proved by an examination of the melting-point curve for mixtures of the two compounds (Fig. 3). The following values were obtained:

Melting-point Curve of Mixtures of $\gamma\gamma$ -Dipyridyl and *s*-Trinitrobenzene.

<i>s</i> -Trinitro- benzene, molecular percentage.	$\gamma\gamma$ -Dipyridyl, molecular percentage.	F. p.	<i>s</i> -Trinitro- benzene, molecular percentage.	$\gamma\gamma$ -Dipyridyl, molecular percentage.	F. p.
100.0	0.0	122.0°	42.3	57.7	110.0
90.7	9.3	111.5	39.4	60.6	108.8
81.4	18.6	102.0	36.3	63.7	107.8
74.4	25.6	99.0	34.1	65.9	106.2
68.8	31.2	102.5	31.9	68.1	104.6
64.0	36.0	106.5	29.2	70.8	101.6
59.8	40.2	109.0	25.6	74.4	98.8
53.7	46.3	110.6	22.4	77.6	94.2
51.5	48.5	111.0	19.1	80.9	93.0
48.8	51.2	111.0	15.1	84.9	95.2
46.8	53.2	110.8	14.0	86.0	100.3
44.5	55.5	110.4	0.0	100.0	112.0

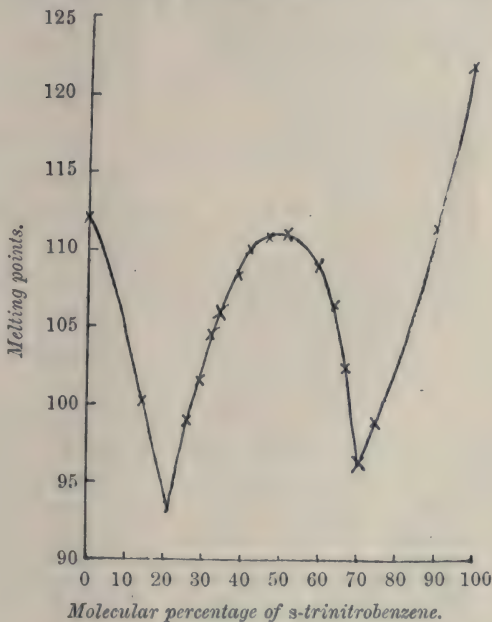
Compound with quinoline, $\text{C}_9\text{H}_7\text{N}, \text{C}_6\text{H}_3(\text{NO}_2)_3$.—Sommerhoff (*loc. cit.*, p. 86) describes a colourless compound containing two molecules of trinitrobenzene to one of quinoline, which was prepared by fusing together the two components and allowing to cool. We

find that when equimolecular quantities of the two compounds are gently warmed together, and the mass allowed to cool, a hard solid, melting at about 75° , is obtained. The compound is practically colourless, and has a strong odour of quinoline. The product obtained from two molecules of trinitrobenzene and one of the base has not a sharp melting point, and is evidently a mixture.

The compound with isoquinoline, $C_9H_7N, C_6H_3(NO_2)_3$, prepared in a similar manner, is also practically colourless, and melts at $87-88^{\circ}$. *o*- and *p*-Toluquinolines and quinaldine yield similar compounds.

FIG. 3.

Melting-point curve of $\gamma\gamma$ -dipyridyl and *s*-trinitrobenzene.



All these additive compounds are decomposed by treatment with solvents, and can be isolated only in the absence of solvents.

The compound with α -naphthaquinoline, $C_{13}H_9N, C_6H_3(NO_2)_3$, can be obtained in pale yellow, felted needles, melting at 133.5° , by crystallising an equimolecular mixture of the two components from hot alcohol. From dilute solutions it is deposited in well-developed, yellow, prismatic needles:

0.2044 gave 24.9 c.c. N_2 (moist) at 14° and 744 mm. $N = 14.03$.

$C_{19}H_{12}O_6N_4$ requires $N = 14.28$ per cent.

The isomeric compound with β -naphthaquinoline, which can be

prepared in a similar manner, crystallises in pale buff-coloured needles, melting at 112° :

0.2015 gave 24.4 c.c. N_2 (moist) at 12° and 744 mm. $N = 14.06$.

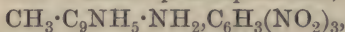
$C_{19}H_{12}O_6N_4$ requires $N = 14.28$ per cent.

The compound with tetrahydroquinoline, $C_9H_{11}N, C_6H_3(NO_2)_3$ (compare Sommerhoff, *loc. cit.*, p. 89), crystallises from alcohol in glistening, black plates, melting at 100° :

0.1838 gave 25.3 c.c. N_2 (moist) at 13° and 764 mm. $N = 16.35$.

$C_{15}H_{14}O_6N_4$ requires $N = 16.2$ per cent.

The compound with *o*-amino-*p*-toluquinoline,

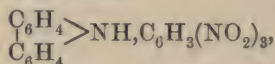


crystallises from alcohol in deep brick-red needles, melting at 139° :

0.5105 gave 0.2857 $C_6H_3(NO_2)_3 = 56.8$.

$C_{16}H_{13}O_6N_5$ requires $C_6H_3(NO_2)_3 = 57.4$ per cent.

The compound with carbazole,



crystallises from hot alcohol in long, orange-red needles, melting at 199.5° :

0.1510 gave 18.7 c.c. N_2 (moist) at 12° and 764 mm. $N = 14.8$.

$C_{18}H_{12}O_6N_4$ requires $N = 14.75$ per cent.

Compound with α -methylindole,

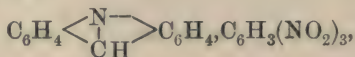


—van Romburgh (*Rec. trav. chim.*, 1895, 14, 67) has described an additive compound of indole and trinitrobenzene. It contains equimolecular proportions of the components, and forms golden-yellow crystals, melting at 187° . We have obtained an additive compound of α -methylindole and trinitrobenzene; it crystallises from alcohol in bright scarlet needles, melting at 151.5° :

0.1987, gave 27.1 c.c. N_2 (moist) at 10° and 772 mm. $N = 16.6$.

$C_{15}H_{12}O_6N_4$ requires $N = 16.3$ per cent.

The compound with acridine,

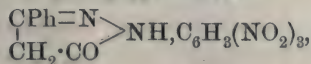


is obtained in stout, amber-coloured needles, melting at 115° , when a mixture of trinitrobenzene and a slight excess of acridine is crystallised from alcohol:

0.2010 gave 24.0 c.c. N_2 (moist) at 10° and 760 mm. $N = 14.3$.

$C_{19}H_{12}O_6N_4$ requires $N = 14.28$ per cent.

The compound with 3-phenylpyrazolone,

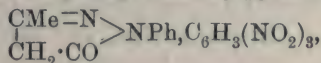


crystallises from a mixture of alcohol and benzene in canary-yellow prisms, melting and decomposing at 198°:

0.800 gave 0.4562 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 57.6$.

$\text{C}_{15}\text{H}_{11}\text{O}_7\text{N}_5$ requires N = 57.1 per cent.

The compound with 1-phenyl-3-methylpyrazolone,



crystallises from alcohol in ruby-red prisms, melting at 92°:

0.4156 gave 0.2244 $\text{C}_6\text{H}_3(\text{NO}_2)_3 = 55.1$.

$\text{C}_{16}\text{H}_{13}\text{O}_7\text{N}_5$ requires N = 55.0 per cent.

VIII.—Non-formation of Additive Compounds.

Sommerhoff states that pyridine, phenylhydrazine, diethylamine, ammonia, azobenzene, *p*-aminophenol, nitro-*o*-toluidine, bromoaniline, diaminoazobenzene, and *o*-anisidine do not form additive compounds with trinitrobenzene. We have been able to show that the last three of these do form additive compounds. Romburgh states that piperidine, pyridine, morphine, quinine, strychnine, and nicotine do not combine with trinitrobenzene.

Our own experiments show that additive compounds of the following compounds with trinitrobenzene cannot be isolated when a solvent such as alcohol is used.

o-, *m*-, and *p*-Aminophenol, *m*-diethylaminophenol, tetrabromophydroxydiphenylamine, acetyl-*p*-phenylenediamine, triphenylamine, and the corresponding triphenylphosphine and triphenyl-

IX.—Molecular-weight Determinations in Benzene Solution by the Cryoscopic Method.

Compound of trinitrobenzene and	Weight of solvent.	Weight of solute.	Δt .	M.	
				Found.	Calculated.
Tetramethyl- <i>p</i> -diaminodiphenylmethane.	15.0	0.1157	0.17	227	467
	15.0	0.2297	0.34	225	467
Ethyl <i>p</i> -aminobenzoate ...	15.0	0.1979	0.35	188	378
	15.0	0.4022	0.71	189	378
<i>p</i> -Tolyl- α -naphthylamine.	15.0	0.1944	0.31	209	659
	15.0	0.3839	0.60	213	659
β -Dinaphthylamine	15.0	0.1886	0.26	242	695
ψ -Cumidine	15.0	0.2000	0.40	167	348
	15.0	0.3900	0.77	169	348
Diphenylamine ..	15.0	0.1943	0.33	196	595
	15.0	0.3969	0.68	195	595

arsine. *m*-Aminobenzoic acid, tribromo-*m*-aminobenzoic acid, hydrazobenzene, diazoaminobenzene, 5-chloro-1-phenyl-3-methylpyrazole, methyldiphenylamine, amarine, and 2:4:5-triphenylglyoxaline.

The formation of these characteristic derivatives with trinitrobenzene or trinitrotoluene can be used for the detection of small quantities of various amines, and it is highly probable that the compounds will prove of use in the purification of a number of different amines, as most of them crystallise remarkably well, are readily obtained in a state of purity, and can, in many cases, be decomposed by means of mineral acids

We desire to express our indebtedness to Messrs. Levinstein, Ltd., Professor Orton, Dr. G. T. Morgan, and Dr. J. F. Thorpe, for kindly providing us with specimens of amines, and to the Research Fund Committee of the Chemical Society for a grant in aid of this investigation.

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ABERYSTWYTH.

LIV.—*Some New Metallic Carbonyls.*

By the late LUDWIG MOND, F.R.S., HEINRICH HIRTZ, and
MATTHEWMAN DALTON COWAP.

Introduction by Robert Ludwig Mond.

My father, the late Dr. Ludwig Mond, had his attention drawn to the possible existence of compounds of carbon monoxide and various metals by the examination of a peculiar black deposit, which had formed on some nickel valves used in his ammonia-soda process, which he described in his Presidential Address to the Chemical Section of the British Association in 1896. The examination of this black compound (a carbide of nickel), which was conducted in his private research laboratory by his assistants, Dr. Carl Langer and Dr. Friedrich Quincke, led to the discovery of a volatile compound of nickel and carbon monoxide, the properties of which were described in 1890 (Trans., 57, 749). Further research led to the discovery of ferropentacarbonyl and diferroheptacarbonyl (Mond and Langer, Trans., 1891, 59, 1090), and although numerous experiments were made to obtain similar compounds with other metals, they led at that time to no success.

The study of these compounds and the technical application of the nickel carbonyl process monopolised the time of Dr. Mond and his staff to the exclusion of further scientific research in this direction.

The low-temperature research work carried on by Sir James Dewar at the Royal Institution, in which Dr. Mond took a very great interest, led him to suggest to Sir James Dewar to examine the action of carbon monoxide on nickel at high pressures. The result of this work is embodied in a patent taken out by Sir James Dewar on behalf of my father in 1902, and the comparative facility with which the reaction proceeded at a higher pressure led my father to instal a high-pressure plant at his private laboratory for the further study of this problem. On the conclusion of the experiments for obtaining the technical data of a high-pressure process, he directed his attention once more to studying the behaviour of other metals when subjected to the action of carbon monoxide under these high pressures, and it was chiefly to this research that he devoted the time and thought he could afford for scientific research during the latter years of his life.

The present paper was drawn up on Dr. Mond's instructions to be read before the Chemical Society, and although he did not see it in its finally revised form, he was fully conversant with all the experiments and the results obtained. The actual researches presented great difficulties, both of a technical and theoretical nature, and were very ably carried out by my father's assistants, Dr. Heinrich Hirtz and M. Dalton Cowap, acting under my father's instructions, or my own when my father was absent.

R. L. M.

The following table gives a résumé of the present state of knowledge of the different compounds of the metals with carbon monoxide.

All these carbonyls have very similar chemical properties; thus, when heated, they all decompose into carbon monoxide and the metal, which is deposited in the form of a bright metallic mirror. They are not attacked by non-oxidising acids, but are quickly dissolved by oxidising acids, and especially by aqueous solutions of the halogens, with the evolution of carbon monoxide. At least one of the carbonyls of each metal is volatile without decomposition, and can be purified by distillation or sublimation. They are all more or less soluble in the usual organic solvents, such as ether, ethyl alcohol, benzene, oils, etc., and are all insoluble in water.

Table of Physical and Chemical Properties of Carbonyls.

	Formula.		Sp. gr.	Melting point.	Boiling point.	Vapour pressure.	Colour.	Formation.	Decomposition.
	Empirical.	Molecular.							
Ni.	Ni(CO)_4	Ni(CO)_4	1.32446 at 14°	-25°	+43°/751 mm.	238 mm. at 15°	Colourless liquid	Ni and CO at ordinary pressure.	To Ni and CO (partial) at 0° in a vacuum and at 50° under ordinary pressure; no intermediate products could be found.
Co.	Co(CO)_4	$\text{Co}_2(\text{CO})_8$	1.73	+51°	Decomposes above 52°	0.072 mm. at 15°	Orange crystals	Co and CO at min. of 40 atm. and 150°.	To Co and CO (complete) above 60°; to Co(CO)_5 and CO between 50° and 60°. No recombination at 0-60°.
Fe	Fe(CO)_5	?	?	Decomposed above 60°		—	Black crystals	From Co(CO)_4 at 60°.	To Co and CO above 60°; no intermediate products could be found.
	Fe(CO)_5	Fe(CO)_5	1.4064 at 18°	-21°	102.8°/749 mm.	25.9 mm. at 16.1°	Yellow liquid	Fe and CO at high pressure and temp. From Fe(CO)_5 by distilling in CO.	To Fe(CO)_5 and CO by light; to Fe and CO by heating vapours.
	$\text{Fe}_2(\text{CO})_9$?	2.085 at 18°	Decomposed at 100°		Not measurable	Gold coloured crystals	Fe(CO)_5 by light. From Fe and CO by light.	To Fe(CO)_5 and CO and Fe by heating to 100°; to Fe(CO)_4 and Fe(CO)_5 by heating solution to 95°.
	Fe(CO)_4	Very high	1.986 at 18°	Decomposed at 140-150°		—	Green crystals	From Fe(CO)_5 by heating in solution at 95°.	To Fe and CO by heating to 150° or above. No recombination to Fe(CO)_5 or Fe(CO)_9 by CO; pressure up to 150 atm.
Mo.	Mo(CO)_6	?	1.96 at 15°	Volatilises before melting		?	White crystals	Mo and CO at a minimum of 130 atm. and 200°.	To Mo and CO by heating to above 150°.
Ru.	?		?	?	?	?	Rose to orange	Ru and CO at a minimum of 400 atm. and 300°.	To Ru and CO by heating.

"Some physical properties of nickel carbonyl" (Mond, Langer, and Quincke, *Trans.*, 1890, 57, 749); "Studi sul nichel tetracarbonile" (Mond and Nasini, *Atti R. Acad. Lincei*, 1890, 7, 1, 411); "Ueber einige physikalische Eigenschaften des Nickel-tetra-karbonyls" (Mond and Nasini, *Zeitsch. physikal. Chem.*, 1891, 8, 150); "On nickel carbon oxide and its application in arts and manufactures" (Mond, *Brit. Assoc. Rep.*, 1891); "Metallic carbonyls" (Mond, *Roy. Inst. Lecture*, June and 1892); "The history of my process of nickel extraction" (Mond, *J. Soc. Chem. Ind.*, 1896, 14, 946); "The extraction of nickel from its ores by the Mond process" (Roberts-Austen, *Proc. Inst. Civil Eng.*, 1898-1899, 135, Pt. 1); "Ueber die chemische Dynamik des Nickelkohlenoxyds" (Mittasch, *Zeitsch. physikal. Chem.*, 1902, 40, 1); "Einige Beobachtungen über Lösungsvermögen und elektrische Leitfähigkeit von flüssigem Nickelkohlenoxyd" (Mittasch, *ibid.*, 1903, 46, 37); "Some physical properties of nickel carbonyl" (Dewar and Jones, *Proc. Roy. Soc.*, 1903, 71, 427); "The toxicology of nickel carbonyl" (Armit, *J. Hygiene*, 1907, 7, 525); "Note on a volatile compound of cobalt with carbon monoxide" (Mond, Hirtz, and Cowap, *Brit. Assoc. Rep.*, 1908, 98, 165); "Ueber eine flüchtige Verbindung des Eisens mit Kohlenoxyd" (Mond and Quincke, *Ber.*, 1891, 24, 2248); "Note on a volatile compound of iron with carbon oxide" (Mond and Quincke, *Trans.*, 1891, 59, 404); "On iron carbonyls" (Mond and Langer, *J. Soc. Chem. Ind.*, 1891, 10, 1040); "The physical and chemical properties of iron carbonyl" (Dewar and Jones, *Proc. Roy. Soc.*, 1905, 4, 76, 568); "On a new iron carbonyl" (Dewar and Jones, *Proc. Roy. Soc.*, 1905, 4, 76, 568); "On the action of light and on the action of heat on the iron carbonyls" (*ibid.*, 1907, 4, 79, 66).

The physical properties, however, vary very considerably, from nickel tetracarbonyl, a liquid which is very easily volatile and has a specific gravity of 1.32, to the non-volatile diferrononacarbonyl, with a specific gravity of 2.085. Some can be obtained in the form of gas, liquid, or solid; others as a solid and gas; and others still only in the solid state. The colour varies from black to white through almost the whole spectrum. Owing to the various composition of these compounds, it is extremely difficult to construct a general chemical formula for them, but as they have such a similar chemical behaviour they must be constituted in a similar manner. One cannot regard all the carbonyl groups as being combined directly with the metal, as that would involve cobalt being sexa- and octa-valent, iron octa-, nona-, and deca-valent, and so on. Also, ring-formation, as hitherto supposed, does not explain all the properties; for instance, if nickel carbonyl has the con-

stitution $\text{Ni} \begin{smallmatrix} \diagup \text{CO} \cdot \text{CO} \\ \diagdown \text{CO} \cdot \text{CO} \end{smallmatrix}$, cobalt tetracarbonyl should have a similar

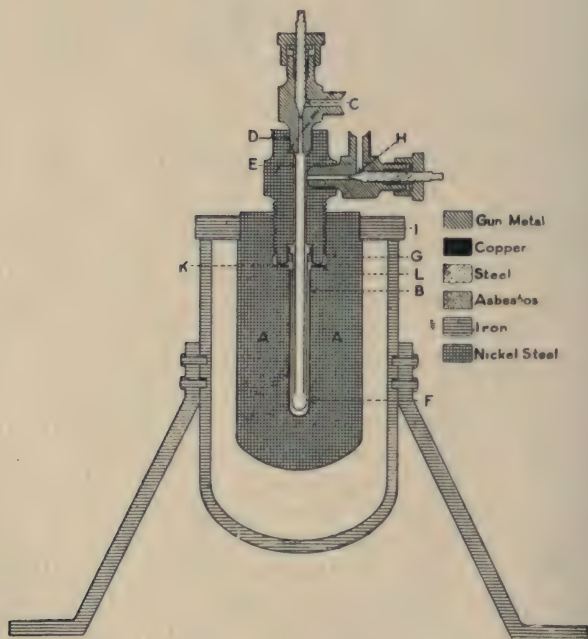
constitution, namely, $\text{Co} \begin{smallmatrix} \diagup \text{CO} \cdot \text{CO} \\ \diagdown \text{CO} \cdot \text{CO} \end{smallmatrix}$; but in this case it is difficult

to understand why it has double the molecular weight in benzene solution, and, moreover, such a constitution does not explain why one carbonyl group should be more easily eliminated than the rest. Further, diferrononacarbonyl cannot thus be brought into line with the other carbonyl compounds. In the case of molybdenum carbonyl one would have to assume the formation of a ring containing seven atoms, which can be formed only with great difficulty among organic compounds. Consequently, we are at present of the opinion that these compounds have a molecular rather than an atomic constitution, similar to the hydrates of salts or of acids, the carbonyl group taking the place of the water of crystallisation or hydration. Here again, however, the difficulty arises that we have to assume that these compounds, although they can be obtained in a gaseous form, and so far as they could be investigated therein, have a normal gas density, exist in the gaseous state also in this molecular condition. This would be quite an unusual property, but, in our opinion, not more difficult to assume than the fact that many organic compounds have, at a temperature slightly above their boiling points, an abnormally high vapour density, and also that gaseous sulphur exists in the form of S_8 , S_6 , and S_2 , according to the temperature and pressure.

EXPERIMENTAL.

In a previous paper read before the British Association and published in the *Chemical News* of October 2nd, 1908, we have described the formation of a cobalt carbonyl, and at the International Congress of Applied Chemistry, London, 1909, Dr. Mond, in his Presidential Address to Section II, announced the formation of a new cobalt carbonyl and also the formation of a molybdenum and ruthenium carbonyl. We now give some further details on the formation and properties of these compounds.

FIG. 1.



The apparatus which we used for these experiments consisted of a nickel-steel tube, which could be heated up to 450° and subjected to a pressure of upwards of 500 atmospheres. The details of the construction of this retort are shown in Fig. 1. *A* represents the retort, which is copper-lined at *B* so as to prevent the carbon monoxide from attacking the iron of the retort. The gas enters the retort at the pressure valve *C*, fixed to the retort by a cone-joint *D*. Brazed into the bottom part of the joint *D* is a copper tube *E*, which reaches to the bottom of the retort. The

gas penetrates through the material, which is contained in a glass tube *P*, this tube being loosely held in the top of the retort by a gun-metal nipple *G*. The gas then leaves the retort at the outlet valve *H*. The cover, together with the copper and glass tube, is screwed into the body of the retort at *I*, and the joint is made by a metal ridge *K*, which protrudes from the bottom part of the screw *I*. It was found necessary to add a copper washer *L*. With this arrangement the retorts could be kept tight up to 500 atmospheres' pressure and a varying temperature up to 450°. The carbon monoxide was compressed by a two-stage compressor into a cylinder, from which it was taken to the inlet valves of the retorts; the gases were then led through the retort, and from the exit they passed through a glass tube, cooled in a freezing mixture, and then through another glass tube, heated so that a metallic mirror could, if possible, be formed, which could then be analysed.

Cobalt Carbonyl.

The preparation of cobalt carbonyl, $\text{Co}(\text{CO})_4$, was carried out by the following method. Cobalt oxalate was carefully heated until it was completely converted into oxide. This was thoroughly washed free from chlorides, which we found to be detrimental to the formation of the carbonyl. The oxide was then dried at about 120°, filled into the glass tube of the retort, and the whole apparatus was screwed together. The cobalt oxide was reduced to cobalt by a current of hydrogen at 300° under 5 atmospheres' pressure, and, after reduction, the hydrogen was displaced by carbon monoxide and the temperature lowered, whilst the pressure was increased. The minimum pressure necessary for the formation of cobalt carbonyl was found to be between 30 and 40 atmospheres at a temperature of about 150°. The higher the pressure the more rapid is the formation of the carbonyl, but we are not as yet prepared to say how far the pressure may be raised. We have prepared cobalt carbonyl under 30, 50, 100, 200, and 250 atmospheres' pressure, and at a temperature varying with the pressure from 150° to 220°, obtaining fine orange-coloured, transparent crystals of the composition $\text{Co}(\text{CO})_4$. Some of the properties have been described already in the above-mentioned paper. We repeat these here with some corrections and additions. The crystals are best preserved by sealing them in a glass tube in an atmosphere of hydrogen or carbon monoxide. When they are left in contact with the atmosphere, decomposition takes place, a deep violet substance consisting of a basic cobalt carbonate being left behind. Cobalt carbonyl is very slowly attacked by non-oxidising acids, such as hydrochloric or sulphuric, whereas when

nitric acid or bromine is present, the reaction is accelerated considerably, and the corresponding cobalt salt is formed with the elimination of carbon monoxide, according to the equation $\text{Co}(\text{CO})_4 + \text{Br}_2 = \text{CoBr}_2 + 4\text{CO}$. Cobalt carbonyl is insoluble in water, but more or less soluble in organic solvents, such as carbon disulphide, ether, naphtha, alcohol, and also in nickel carbonyl. If these solutions are kept for some time, or if they are warmed, decomposition ensues.

The specific gravity measured by the suspension method at 18° is 1.73, but we do not yet regard this figure as final, for, if the substance is kept only for a few hours, the specific gravity increases considerably, owing to decomposition. The molecular formula was determined by the cryoscopic method, which gave the molecular weight of 328, corresponding practically with $\text{Co}_2(\text{CO})_8$. The vapour pressure could not be directly measured owing to decomposition; we therefore employed a method by which it was possible to estimate it as follows. Pure carbon monoxide was passed over the crystals at a rate of about half a litre per hour at a temperature of 23 – 25° . The gas volatilised the crystals to a certain point, and this partly saturated gas was passed through a coil which was kept exactly at 15° . The excess of cobalt carbonyl which the gas had absorbed at 23 – 25° over that which it could keep in a gaseous state at 15° was deposited in the cooling coil in the form of fine crystals, so that the gas leaving the coil was quite saturated at 15° . Care was taken that the room-temperature was well above 15° during the experiment. The carbon monoxide, saturated with gaseous cobalt carbonyl, was now passed through bromine-water in a series of absorption bulbs, and the cobalt retained by the bromine-water was estimated by analysis. It was found that 42.58 litres of carbon monoxide had taken up 10.6 milligrams of cobalt or 4.01 c.c. of cobalt carbonyl vapour, corresponding with 0.0944 c.c. per litre (0.0094 per cent. by volume). This corresponds with a vapour pressure of 0.072 mm. at 15° . This low value is very remarkable, as the vapour pressure of nickel carbonyl under these conditions is about 200 mm.

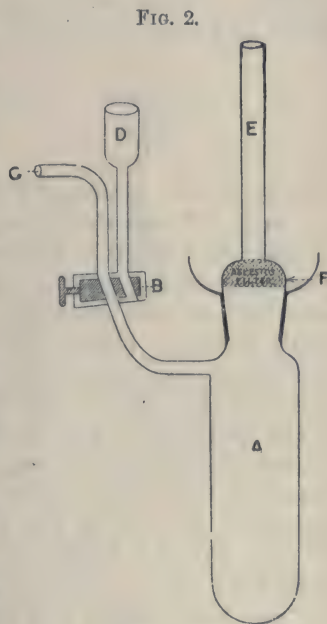
The pure crystals melt, without decomposing, at 51° . Very slow decomposition sets in immediately after melting, and the decomposition is quite appreciable at 53° . At 60° the decomposition is fairly rapid, so that the compound is entirely decomposed at this temperature in about two working days. It was found that exactly one-quarter of the carbon monoxide present in the carbonyl was eliminated, as is shown in the following table:

Co(CO) ₄ taken (milligrams).	Co found (milligrams).	CO (A) given off at 60° (milligrams).	CO (B) in compound (milligrams).	CO/Co in molecular proportion.	B/A.
239.0	82.3	38.8	—	1.006	—
154.4	53.8	25.2	—	1.003	—
calculated					
141.0	—	23.4	93.0	—	3.98

The amount of gas given off was measured at short intervals, and a curve (see Fig. 3) was drawn showing the rate of decomposition of cobalt carbonyl at 60°. From this curve we conclude that there is no further stage of decomposition between the compound Co(CO)_4 and the compound Co(CO)_3 .

The new compound, *cobalt tricarbonyl*, Co(CO)_3 , was purified and analysed as follows. It was dissolved in warm benzene, and, on cooling the solution, the substance separated in jet black crystals. These were collected, dried, and decomposed with bromine-water. The carbon monoxide evolved and the cobalt remaining were estimated by the usual methods. It was extremely difficult to obtain this compound sufficiently pure for analysis, as it is so very easily changed in air.

The apparatus used for this analysis is shown in Fig. 2. *A* is the crystallisation and decomposition vessel. It is connected at one side with a two-way cock *B*. Through *C* an inert gas, such as hydrogen or carbon dioxide, could be passed through it, and at *D* the bromine-water could be added. On the top was ground in another tube *E*, which could be fitted with an asbestos



filter *F*. The two-way cock and the top tube were fitted with a mercury seal, so that a complete vacuum could be obtained. The cobalt tetracarbonyl was then decomposed in a separate vessel at 60°. The residue was dissolved in warm benzene in an atmosphere of hydrogen and filtered into the vessel *A*, tube *E* being meanwhile removed. The filter was composed of asbestos-wool contained in a dropping funnel, in which an atmosphere of an inert gas was maintained. During filtration and crystallisation a current of inert gas was passed through the apparatus. When the warm benzene

solution was in the vessel, the apparatus was cooled in ice-water until all the benzene was frozen. Tube *E* was now inserted, the apparatus reversed, the benzene slowly thawed, and passed through the filter. The crystals of cobalt tricarbonyl remained in *A* or at *F*. Dry inert gas was now passed through the apparatus at the ordinary temperature until the crystals were quite dry. Tube *E* was then melted off. The apparatus was then reversed again, mercury poured into the seals, and the apparatus evacuated completely with a good mercury pump. Then bromine-water was poured into *D* and carefully brought into the vessel. This was gently heated, and sufficient bromine added until its vapour was just visible in *E*. The vessel was again evacuated, and the gas collected was measured and analysed. The cobalt was determined in the liquid. The following table shows the proportion of cobalt to carbon monoxide found in cobalt tricarbonyl:

Co (milligrams).	CO (milligrams).	CO/Co in molecular proportion.
48.6	67.3	2.93
75.7	107.3	2.99

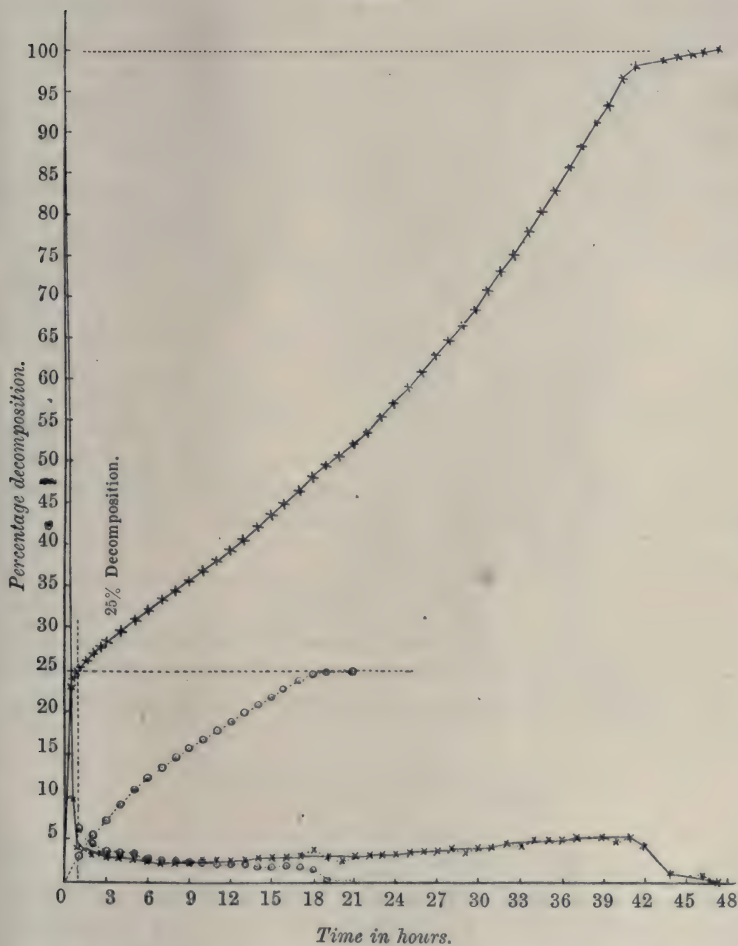
It is interesting to notice the further decomposition of the tetracarbonyl. 0.1600 Gram was decomposed at 100°, and the gas evolved was read off at first every fifteen minutes, then every hour. Almost at once a quarter of the carbon monoxide was liberated, then the reaction suddenly slowed down, and continued fairly evenly for twelve hours, when the reaction slowly accelerated again, until between the thirty-sixth and the forty-first hour (the maximum speed) of the reaction was about twice as quick as at the sixth to the ninth hour (the minimum). After the forty-second hour the reaction diminished very suddenly, and was practically completed at the forty-seventh hour, when 99.6 per cent. of the theoretical amount of gas had been given off (see Fig. 3). At 80° and 90° the decomposition was very similar, but proceeded much more slowly. An explanation of this strange behaviour has not yet been found, but from very numerous experiments the following rules can be deduced.

Influence of the Decomposing Vessels.—The larger the volume, the slower is the decomposition. In small vessels the decomposition proceeds comparatively quickly, and no increase of speed could be detected. In comparatively large vessels the decomposition is very slow, and only a slight increase towards the end could be noticed.

Influence of Pressure.—A pressure of 2 atmospheres did not influence the decomposition. In a vacuum the decomposition takes place much more quickly; no increase towards the end could be

detected. No re-combination of the products takes place between 15° and 60° whether the decomposition of the carbonyl was complete or whether 25 or 50 per cent. of the theoretical amount of carbon

FIG. 3.



—*—*—*— (Upper): Decomposition of cobalt carbonyl at 100° .
 ---○---○---○--- " : " " " " 60° .
 —*—*—*— (Lower): Hourly rate of the decomposition (multiplied by 2) at 100° .
 ---○---○---○--- " : " " " " " " 60° .

monoxide had been given off. We have not yet been able to establish any relation between the tricarbonyl and hexahydroxybenzene or any other organic compound; neither were we able

to estimate the molecular weight of the tricarbonyl, as the solubility in the usual solvents is too small.

Nickel Carbonyl.

After having carried out the above experiments with cobalt, nickel tetracarbonyl was investigated in the hope of obtaining a compound similar to cobalt tricarbonyl, but so far we have not succeeded in doing so. We endeavoured to decompose nickel tetracarbonyl in an almost complete vacuum at 0° , also by decomposing it in a small vessel fitted with a reflux condenser at 50° , and by subjecting nickel (prepared by reduction) or nickel tetracarbonyl to the action of carbon monoxide under a pressure of 120 atmospheres. Incidentally it was found that when carbon monoxide containing oxygen and nickel carbonyl in molecular proportions is heated to 200° , a colloidal nickel oxide is formed. This is deposited on the heated glass tube, through which the mixture is slowly passed, and forms a yellowish-green layer on the tube; it separates in small flakes having the physical appearance of dried varnish, and if the layer is sufficiently thin it gives beautiful iridescent colours. It is soluble in acids, even in aqua regia, only with great difficulty on prolonged boiling. When heated in hydrogen it forms a nickel mirror.

Iron Carbonyl.

The liquid ferropentacarbonyl is formed under a pressure of 150—250 atmospheres, and at a temperature of 180 — 220° , without the aid of light. We have not yet succeeded in decomposing this compound.

Molybdenum Carbonyl.

In the case of molybdenum the great difficulty has been to prepare metallic molybdenum in a sufficiently active form. The reduction of the oxides with hydrogen is quite useless, because the temperature at which the reduction takes place is too high to leave the molybdenum in an active state. It is necessary first to prepare an oxychloride by heating a strong solution of molybdenum in nitric acid repeatedly with hydrochloric acid. The oxychloride is then reduced by hydrogen at a low temperature. The molybdenum prepared in this way is not very active; it is just pyrophoric if gently warmed. It was subjected to the action of carbon monoxide at a minimum pressure of 150 atmospheres and at a temperature of about 200° . Under a pressure of about

200—250 atmospheres, a very small quantity of crystals was slowly formed in the cooled glass tube.

Molybdenum carbonyl forms highly refractive, white crystals; the specific gravity measured by the suspension method is 1.96, and it is soluble in ether or benzene. The crystals evaporate before melting, and can easily be sublimed in an atmosphere of hydrogen or carbon monoxide at a temperature of 30° or 40°. The vapours begin to decompose at 150°. The chemical properties resemble those of the other carbonyls. It is scarcely attacked by non-oxidising agents, but quickly by oxidising agents, especially by bromine; carbon monoxide is eliminated, and molybdic acid is left in suspension. Analysis of the crystals gave the following result:

Found, CO=0.0432 gram. Mo=0.0279 gram.

This corresponds very nearly with a molecular proportion of CO: Mo=6: 1. The formula is therefore $\text{Mo}(\text{CO})_6$.

Ruthenium Carbonyl.

If ruthenium black is subjected to the action of carbon monoxide, a very small quantity of a yellow-orange deposit is formed in the cooled glass tube, and a comparatively strong mirror is formed in the heated glass tube. The reaction does not start below a pressure of about 350—450 atmospheres, and a temperature of 300°. The deposit is insoluble in hydrochloric acid, but soluble in nitric acid or bromine, gas being evolved. It contains ruthenium, and forms a ruthenium mirror when heated.

The mirror obtained in the heated glass tube is soluble to a slight extent in hydrochloric acid (solution contains iron). The insoluble part is not dissolved by aqua regia, and consists of ruthenium. Although the quantity hitherto obtained is too small for analysis, we can conclude from the formation of a ruthenium mirror that a ruthenium carbonyl has been produced.

Other Metals.

We have also investigated the action of carbon monoxide on other metals, such as manganese and chromium, which, however, we had great difficulty in obtaining in a suitable pyrophoric form. Reduction of the oxides with hydrogen does not occur even under a pressure of 300 atmospheres and at the temperatures we were able to employ. We obtained these metals in a highly pyrophoric state, however, by Fereé's method, which consists in distilling their amalgams in a high vacuum; we also succeeded in preparing them quite free from mercury. Even under pressures up to 500 atmospheres and at temperatures up to 450°, however, we did

not observe the least deposit in the cool tube or any mirror in the heated glass tube.

In the case also of tungsten (prepared by reducing the oxides or chlorides with hydrogen or by reducing the oxides with zinc or sodium), no indication of the formation of a carbonyl occurred, although the metal obtained by reducing the oxide with sodium was very much more active than any other form; it was, however, not pyrophoric.

Palladium and rhodium, prepared in the form of black by different methods, also gave no result.

The investigation is being continued.

LV.—*The Densities and Molecular Weights of Neon and Helium.*

By HERBERT EDMESTON WATSON.

IN recent years, the atomic weights of a large number of the elements have been determined with the greatest possible care, thereby affording material for testing the various theories which have from time to time been brought forward to account for the relations evidently existing between the atomic weights of the various elements. Special attention has been paid to two very well-defined groups in the Periodic Table, namely, the alkali metals and the halogens, but at present it cannot be said that any definite connexion has been found between the values obtained. Now, the rare atmospheric gases form a group at least as well defined as the two just mentioned, and, moreover, one which lies directly between them, so that a series of accurate atomic weight determinations for these elements would fill a considerable gap in the present data, and might lead to important results.

In addition to this, the gases in question are, to the best of our knowledge, monatomic, and consequently more simple in their constitution than the other permanent gases, so that a close study of all their properties should be invaluable to the development of the kinetic theory. A number of calculations of molecular properties of the monatomic gases have recently been made (Rudorf, *Ann. Physik*, 1909, [iv], **29**, 751; 1910, **31**, 416; *Phil. Mag.*, 1909, [vi], **17**, 795; Happel, *Ann. Physik*, 1904, [iv], **13**, 340; 1906, **21**, 342; 1909, **30**, 175), but the results are mostly discordant. This is probably in many cases caused by inaccuracy in the available data, but at the same time it shows very clearly in how many

respects the Kinetic Theory is lacking, and if this is the case for the simplest bodies with which we are acquainted, it does not seem likely that much true knowledge can be obtained by applying the hypotheses of the theory to more complicated substances, except as a mere approximation.

The gas about which, perhaps, least of all is known is neon, for since its original isolation it has never again been prepared in the pure state. Recently, however, M. Claude, of Paris, has designed an apparatus for producing considerable quantities of the lighter constituents of the atmosphere (*Compt. rend.*, 1908, **147**, 624), and owing to his kindness in presenting Sir William Ramsay with about 40 litres of the product, which contained approximately 45 per cent. of mixed helium and neon, an opportunity has been given of isolating a large amount of the latter gas in a state of purity even greater than that previously attained. The present paper gives an account of the method used, and the results obtained for the density.

It may at the outset be stated that the only real difficulty (apart from manipulation troubles) occurring in the preparation of neon, is its separation from helium. This was originally effected (Ramsay and Travers, *Phil. Trans.*, 1901, **197**, 47) by means of liquid hydrogen, but as it is difficult to obtain a constant supply of this substance, it was decided to investigate the other possible methods of separation, which are two in number, namely, diffusion through quartz, and fractionation from charcoal at low temperatures.

The Diffusion of Helium through Quartz.

While making experiments with a helium thermometer at high temperatures, it was noticed by Jaquerod and Perrot (*Compt. rend.*, 1904, **139**, 789; *Arch. sci. phys. nat.*, 1904, [iv], **18**, 613) that quartz at about 1200° is very permeable to helium, 85 per cent. of the gas diffusing through the walls of the thermometer in six hours, and the rate of diffusion being approximately proportional to the pressure.

In order to see if advantage could be taken of this property to separate helium from neon, the following experiment was performed. A quartz combustion tube was connected with two gas-holders containing neon and helium in the proportions in which they exist in the air, so that the gas could be circulated through the tube. A second, very thin quartz tube, closed at one end, and terminating in a capillary at the other, was fitted inside the first, and connected with a Töpler pump. The tubes were heated to the highest temperature attainable with an ordinary gas combustion furnace for about six hours, a vacuum being maintained in the

inner tube, but only a small quantity of gas could be pumped off. Moreover, the total quantity of gas had not appreciably changed in volume, so that the helium had not passed out into the air.

The gas furnace was then replaced by an electric furnace, and the temperature kept at 1200° for about three hours. The rate of diffusion was rather greater than before, but it was soon evident that the method was of no practical use for separating neon and helium.

The gas obtained was freed from a trace of air which had leaked in through the rubber connexions, by absorption in charcoal cooled in liquid air. Spectroscopic examination showed the presence of neon as well as helium, but apparently only in very small quantities. However, the very fact that neon was present is sufficient to show the impossibility of obtaining pure neon in this way, for as soon as the partial pressure of the helium in a mixture became low enough, the rate of diffusion of the two gases would be the same.

The area of the surface of the inner tube was 62 sq. cm., and its thickness approximately 0.35 mm. At 1200° about 1 c.c. of helium diffused through the walls in three hours, the partial pressure being rather more than one-quarter atmosphere. It follows that the quantity of helium which will diffuse in one hour through 1 sq. cm. of quartz 1 mm. thick at 1200° under a difference of pressure of 1 atmosphere, is roughly 0.007 c.c. This result appears to be of quite a different order from that obtained by Jaquerod and Perrot (*loc. cit.*). A possible explanation may lie in the fact that the quartz in the two cases had been differently treated, that used in the present case having been obtained from The Silica Syndicate, London, but such a wide divergence is hardly to be expected.

Fractionation by Means of Charcoal.

It is known that neon undergoes a considerable absorption by charcoal at the temperature of liquid air, whilst helium is scarcely affected in the same circumstances. This property was used by Sir William Ramsay (*Proc. Roy. Soc.*, 1905, A, **76**, 111) when estimating the amounts of these gases in the atmosphere, although the separation was not complete, as the absorbed neon has a considerable vapour pressure. It should, however, be quite possible to obtain pure neon from the mixture.

A few preliminary experiments were first made in order to obtain some idea as to the amount of absorption. A small bulb containing cocoanut charcoal absorbed a comparatively large quantity of the gas, and, on pumping off, the pressure kept nearly

constant for some time at about 40 mm., indicating that some evolution of gas was taking place. Also, if the spectrum of the gas were examined at intervals during the operation, it was seen that the helium D_3 line always became weaker, and sometimes disappeared altogether, so that a considerable change in the composition of the mixture was evidently taking place.

It was consequently decided to submit the gases to a systematic fractionation from charcoal at liquid-air temperature. Also, since a fractionation can be more thoroughly performed with large quantities of gas owing to the relatively smaller volume of dead space, drying tubes, etc., it was decided to work with a considerable volume, although the labour of manipulation, especially in the early stages, was very great.

The more essential parts of the apparatus used are shown in the figure on p. 817. A , A^1 are bottles fitted with doubly-bored rubber stoppers, through which pass two tubes, one just reaching through, and the other extending to the bottom of the vessel, as in an ordinary wash-bottle. The longer tube is connected by means of rubber tubing to a reservoir of water, and by raising or lowering this, gas can be drawn into, or expelled from, the vessel through the shorter tube. This simple form of gasholder was found very convenient for dealing with large quantities of gas, and, moreover, being connected to the rest of the apparatus by rubber joints, could be quickly exchanged or replaced by a smaller bottle when necessary without appreciable loss of gas.

Connected with A , A^1 were drying tubes containing calcium chloride and phosphoric oxide, also a tube of copper oxide, which was continually kept at red heat during the operations to remove hydrogen. B is the charcoal bulb, which was constructed in such a way that the gas passed right through the charcoal as it was drawn from one gasholder to the other.

The size of all these portions of the apparatus was varied as necessary. The first bottles held about 10 litres of gas, and the charcoal bulb had a capacity of 300 c.c., and contained 200 grams of cocoanut charcoal. In the final stages, the bottles were replaced by mercury gasholders similar to H , the drying tubes were omitted, and the charcoal bulb contained only one or two grams of charcoal, the apparatus being used merely for removing last traces of nitrogen and hydrogen. The later fractionations were performed with the aid of the bulb D , which contained 10 grams of charcoal, and was capable of absorbing nearly a litre of neon at atmospheric pressure.

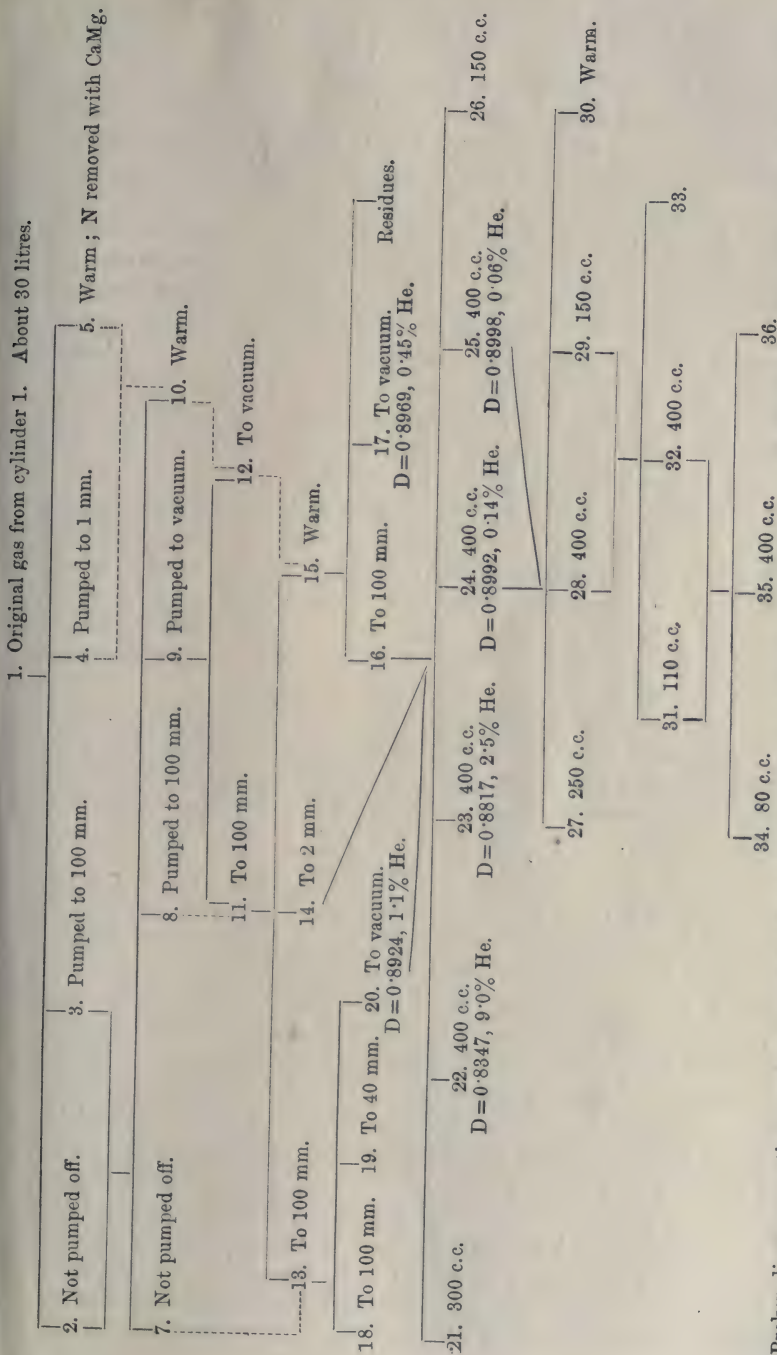
In performing a fractionation, the gas was passed over the cooled charcoal until no more absorption occurred. The charcoal

bulb was then cut off from the rest of the apparatus by means of the screw clips *C*, and the gas pumped off and collected in various fractions according to circumstances. Owing to the volume of some of the early fractions, this process had to be repeated several times, as the charcoal would not absorb sufficient gas in one operation.

The following diagram indicates the method by which the fractionations were performed, and is self-explanatory; for example, fraction 1 was divided up into: fraction 2, which was merely passed over the charcoal and never pumped off; fraction 3, which was pumped off until the pressure sank to 100 mm.; fraction 4, which was pumped off until the pressure reached 1 mm.; and, finally, fraction 5, which was obtained by allowing the charcoal to grow warm, and which naturally consisted mainly of nitrogen.

It is by no means to be considered that the above scheme of fractionation is the best or quickest method of obtaining pure neon from the given mixture, but it must be remembered that at first the actual number of bottles of gas was large, and a systematic series of density determinations would have involved a great deal of labour, without, perhaps, giving very much information as to the right method of procedure. The spectroscopic test served as a rough guide in the early stages, and the variations in pressure while the gas was being pumped off also helped to indicate the quantity of neon, so that the purity of each sample was fairly well known.

As before mentioned, it was observed that if a charcoal bulb containing neon at atmospheric pressure were gradually pumped out, the pressure fell regularly to about 40 mm., at which point it remained nearly constant for some time, and then fell again to approximately 0.05 mm., and naturally, at this low pressure, it was practically impossible to pump off the entire quantity of gas. If the charcoal were then allowed to become warm, a further quantity of gas was always obtained. From this it would seem that neon in contact with charcoal at the temperature of liquid air exerts a more or less definite vapour pressure, provided that sufficient gas be present. If by continual removal of gas the pressure is reduced below this amount, the evolution of gas continues, but more slowly, the behaviour being precisely analogous to that of a compound, such as calcium carbonate, which exerts a definite dissociation pressure until completely decomposed. The slow evolution of gas at low pressures is probably a diffusion phenomenon, for it is known that the structure of coconut charcoal is very fine, and consequently, at low temperatures and pressures, diffusion would be very slow. On warming, the gas would naturally be liberated at a much greater rate. Evidence in favour of this



Broken lines connecting numbers indicate that the corresponding fractions were mixed. The figures standing below some of the fraction numbers show the density of the gas and the calculated percentage of helium, the term "density" here, as well as elsewhere throughout the paper, being taken as the weight, in grams, of a normal litre.

hypothesis is given by the fact that if only a small quantity of gas is initially admitted to the charcoal bulb, it can be completely pumped off again. In such a case, any action between gas and charcoal would be almost entirely on the surface of the latter, so that the question of diffusion could hardly arise. The whole matter is of great interest, and it is proposed to investigate it quantitatively as soon as possible.

From the above facts two important practical deductions were made; firstly, that gas pumped off at or below a pressure of 40 mm. would probably contain only a very small proportion of helium; and secondly, that if the gas obtained by allowing the charcoal to become warm were allowed to escape into the air, a considerable quantity of very nearly pure neon would be lost. Consequently, the residues from the first few fractions were freed from nitrogen by passage over a mixture of calcium and magnesium, and the unabsorbed rare gas was added to the rest.

For the fractions 1—26, water was used as the containing liquid, and the gas as it was pumped off was collected in a wide tube connected by rubber tubing to the gasholder, and inverted over the outfall tube of the pump. Fractions 27 and onwards were never allowed to come into contact with water, mercury always being used, and the gas was transferred from pump to gasholder by means of test-tubes.

After the first few fractionations it was found that the helium lines disappeared from the spectrum of the gas, so that it became necessary to take the density of the gas at intervals in order to ascertain its composition, and the method and apparatus used will now be described.

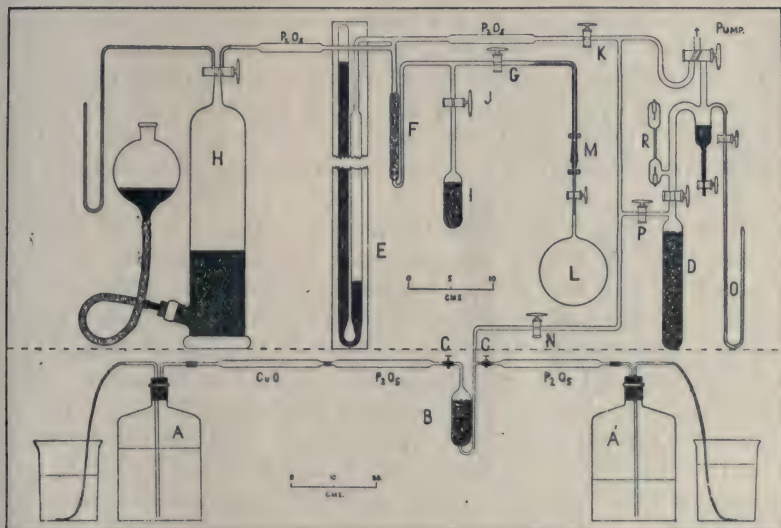
Density Determinations.

The apparatus used for determining densities is shown in the figure. *E* is a barometer furnished with a glass scale. During experiments it was well wrapped up in cotton wool to minimise the effect of draughts, and the temperature taken with two thermometers, one at the top, and the other at the bottom. *F* is a tube packed with glass wool, which was cooled in liquid air during the admission of gas to the bulb, in order to remove mercury vapour. When the requisite pressure in the bulb was reached, the tap *G* was closed, and *F* allowed to become warm, the pressure being brought to the same value as that in the bulb by letting the gas into the gasholder *H*. During an actual determination, the tap *G* was, of course, left open, but any minute traces of impurity in *F* would not have time to diffuse into the bulb.

I is a subsidiary charcoal bulb used for evacuating the density bulb and adjoining parts of the apparatus. It was found ex-

ceedingly tedious to remove the last traces of gas from the density bulb by pumping, owing to the slowness of diffusion at low pressures, and so the method adopted was to pump until only a few cubic millimetres of gas were obtained at each stroke, and then to admit about 10 c.c. of air (or, later, of pure oxygen, which was prepared by heating potassium permanganate in a side-tube not shown in the diagram) to the bulb. This was pumped out to a similar extent, and the process repeated. The tap *J* was then opened, *K* being closed, and the charcoal bulb *I* cooled in liquid air for not less than an hour and a-half. When this method was used, it was found that the weight of the empty bulb remained very constant.

L is the density bulb. It was connected to the rest of the



apparatus by the ground glass joint *M*, which was carefully greased. The grease was washed off with ether before each weighing, and no apparent error was introduced by its use. The weight of the bulb was about 25 grams, its volume at 0° being 297.29 c.c., and at 20° 297.44 c.c. The tap was carefully selected and very lightly greased, all external grease being washed off with ether. No leak was ever detected, and on one occasion upon which the bulb was left evacuated for a month, no increase in weight could be observed.

Some of the experiments were carried out with the bulb at room temperature, in others it was cooled in ice. The disadvantage of the latter method is that the glass is dissolved by the water, and consequently only one value for the weight of the empty bulb is

significant, namely, the one taken after the gas has been weighed and pumped out, and it is far more satisfactory to have two readings as a check on the correct exhaustion of the bulb. It was also found that the weight of the bulb after being wetted was apt to be irregular, probably owing to the disturbance of the surface conditions.

In the experiments at atmospheric temperature, the bulb was encased in a cardboard box, into which were inserted two thermometers, one on each side of the bulb. The whole was then thickly wrapped in cotton wool, and left overnight to come into thermal equilibrium, the tap *G* being turned off for reasons already mentioned. In the morning this tap was turned on, and the movement of the barometer column was always very slight, as might be expected, but about twenty minutes were allowed to elapse before taking any readings in case the temperature of the gas should have been altered by the change of pressure.

It will be seen from the diagram that the purifying bulbs are connected up with the density apparatus and with each other, an arrangement which greatly reduced the labour of transferring the gas, and minimised the risk of contamination. The method of using the apparatus is best seen by means of an example. Suppose, for instance, that it was desired to remove hydrogen from a portion of gas, boil off a first fraction, and take the density of the remainder. The bottles *A*, *A*¹ would be replaced by mercury gas-holders, and the gas transferred to one of them. The drying tubes and the copper oxide tube were evacuated, the tap *N* turned off, and the gas passed over the copper oxide as long as necessary. The taps *N* and *P* were then opened, and the charcoal bulb *D* (previously evacuated) was cooled in liquid air. The gas was expelled from the gasholders, the tap *P* closed, and the residual gas in the connecting tubes pumped off and admitted to the charcoal bulb by the syphon *O*. The charcoal bulb *D* was used for fractionating small quantities of gas in preference to *B*, because there was very little dead space connected with it, and the purity of the gas as regards hydrogen and nitrogen could be seen by means of the spectrum tube *R*.

While the gas was in the charcoal, the tap *N* leading to the purifying apparatus was closed, *K* opened, and all the dead space pumped out with the greatest care, the charcoal bulb *I* being used as an auxiliary to the pump. When all the connecting tubes were completely empty, the light fraction was let into the pump and pumped off. Then, by opening the taps *P* and *K*, and lowering the pressure in the large gasholder *H*, a considerable quantity of gas could be admitted to it from the charcoal bulb. The tap of

the gasholder was then closed, and that of the density bulb opened (*F* being previously cooled in liquid air), thereby still further reducing the amount of gas in the charcoal. Finally, the tap *K* was closed, and the rest of the gas pumped off and transferred by means of test-tubes to *H*, whence it was admitted to the density bulb. When working with pure gas, one test-tube was used exclusively for transferring gas, so as to avoid contamination from air on the walls, and any gasholders were washed out with some of the gas before use.

Calibration of the Apparatus.

To determine the density of a gas, four measurements are necessary, namely, the volume of the density bulb, and the pressure, temperature, and weight of the gas, and the precautions adopted for determining these quantities in the present case will be now briefly given.

The volume of the bulb was determined on two occasions with an interval of over five months between them. One determination was made at 0° , and the other at 16.3° , the bulb in each case being filled with distilled water and then weighed by the method of double weighing. The results were:

Mean weight of water in bulb at 16·3°	297·118 grams
" " " " 0°	297·269 "
Volume of bulb at 16·3°	297·433 c.c.
" " 0°	297·308 "

The coefficient of expansion of glass deduced from these two values is 0.000026, which is quite a usual figure, so that it seems probable that both numbers are correct, and in any case the error would be negligible. The bulb was floated in water before turning off the tap and drying the capillary, so that no correction for distortion arising from the weight of the water is necessary.

The diminution in volume of the bulb on exhaustion was considerable, as the glass was thin. It amounted to 0·089 c.c., the weight of this volume of air being 0·0011 gram. The figure was twice determined, once roughly at the beginning of the experiments by filling the bulb with air-free water, evacuating, and weighing the quantity of water which came past the tap; and once accurately towards the end of the series. For this purpose the bulb was rigidly fixed inside a closed bell-jar completely filled with water, which was in turn immersed in a large sink of water so as to keep the temperature as constant as possible. A long, horizontal capillary tube, also full of water, projected through the cork of the bell-jar, so that any diminution in the volume of the bulb caused the water to move along the tube, the volume of which was afterwards measured. The bulb was evacuated with a Fleuss pump,

and the mean change of volume thus determined. It was found that on evacuation the bulb immediately contracted considerably, but that the contraction continued slowly for about ten minutes. This secondary "creep" was difficult to measure accurately, owing to temperature changes, but as it only amounted to about 3 per cent. of the whole, a small error in it would be quite negligible. A similar effect was also observed on allowing the bulb to expand, and, of course, the extreme contraction was taken as the value required. Two determinations were made, in one of which the bulb was exhausted, and in the other of which it was allowed to fill during the experiment. In both cases, volume readings were taken every minute to eliminate the effect of temperature changes. The distances through which the water moved in the capillary were 384 and 388 mm. respectively, corresponding with a change in volume of 0.089 c.c. The preliminary experiment gave the value 0.085 c.c., but could not be repeated owing to formation of air bubbles.

The pressure of the gas in the experiments was approximately atmospheric, and in all the later ones was adjusted so as to be within a few millimetres of standard pressure. Two short pieces of glass scale by Zeiss, firmly cemented to a strip of plate glass, formed the barometer scale, and readings were taken by means of a telescope, it being possible to read to $1/20$ th mm. The total length was determined by comparison with a standard barometer by Hicks. Several sets of readings were taken on different occasions, and were always found to be consistent. The internal diameter of the tube was 9 mm., and it was sometimes necessary to apply a small correction not amounting to more than 0.1 mm. for the difference in the height of the meniscus in the two arms.

As previously mentioned, some of the experiments were carried out with the density bulb at 0° , and some at room temperature. In the former case the bulb was completely surrounded with finely planed ice, which had been well washed with distilled water. In the latter case, the temperature was determined by means of two thermometers which were graduated in tenths of a degree, and standardised by comparison every two degrees with a Tonnelot thermometer kindly lent by Mr. A. W. Porter, the readings being finally reduced to the hydrogen scale. In order to obtain the density at 0° from these experiments, it was assumed that neon at constant pressure behaves as a perfect gas, the absolute zero being -273.0° , or, in other words, the temperature-coefficient was taken as 0.0036630. The correctness of this assumption will be discussed later.

All weighings were performed on a long beam Oertling balance, which was sensitive to 0.005 milligram with a load of 25 grams.

As might be expected, however, this degree of accuracy was not reached when weighing moderately large glass bulbs, but, nevertheless, if the usual precautions were taken, weights were found not to vary by more than 0.02 milligram, and as the weight of neon in the bulb was usually about 0.25 gram, a small variation in the fifth place of decimals was quite negligible. A dish of calcium chloride was always kept in the balance case, and the density bulb and counterpoise (which consisted of a bulb of almost exactly the same volume, surface, and weight) were usually left overnight before weighing, although no change in weight could be detected after about an hour and a-half. A milligram rider was used, and at least three weighings performed, the rider being placed alternatively on two consecutive divisions of the beam. From the known sensitiveness of the balance, it could at once be seen if any change in weight was in progress, and if this were the case, the weighings were repeated until the weight became constant. The zero was always read after each series of weighings, although it remained perfectly constant for long periods. The bulb and counterpoise were not interchanged, because there was no mechanism for doing this without opening the balance case, and since the only value of a double weighing in a case of this nature is to detect chance irregularities in the length of the balance arms due to unequal expansion, it would be useless to wait until equilibrium was established a second time. A check was, however, applied by weighing two 25-gram weights immediately after taking the zero. The error due to *permanent* inequality of the arms was negligible, a 25-gram weight apparently altering by 0.3 milligram on moving from one pan to the other, so that the correction to the weight of gas (0.25 gram) would only be 0.0015 milligram.

The weights used for weighing the gas were accurately calibrated on an assay balance sensitive to 0.003 milligram. They were also carefully compared with the large weights used for weighing the bulb when full of water, so that the weight of gas is truly expressed in terms of the standard gram. No corrections to the weight in vacuum were applied, for it is not difficult to see that the only effect of this procedure would be to multiply the volume of the density bulb and the weight of the gas by the same factor, in spite of the fact that in one case brass, and in the other case platinum, weights were used. This is due to the fact that the calibration was carried out in air, and no correction then applied for the difference in density of the two kinds of weights (compare Gray and Burt, *Trans.*, 1909, **95**, 1636).

The Purity of the Gas.

As all gases, with the exception of helium, neon, and hydrogen, appear to have no appreciable vapour pressure when in contact with charcoal at the temperature of liquid air, it is quite easy to separate these three from all other gases, it being only necessary to take care that sufficient time for diffusion and subsequent absorption is allowed. One hour is usually long enough when there is not much dead space connected with the charcoal bulb, but in the present experiments the gas was always allowed to remain for two or three hours before finally pumping off. In case of any accidental leak, a sample of the gas was tested before and after each series of experiments by admitting it into the vacuum tube *K* until atmospheric pressure was reached. There are no data as to the amount of nitrogen which can be detected in neon, but 0.01 per cent. can be detected in helium and 0.08 per cent. in argon at a pressure of 1 mm. (Collie and Ramsay, *Proc. Roy. Soc.*, 1896, 59, 268), and the test is far more sensitive at atmospheric pressure. As no trace of the nitrogen spectrum was ever seen in the gas used for density determinations, it seems fairly certain that the quantity present was negligible. The absence of nitrogen ensures that of oxygen.

As other observations appeared to show that argon is not always absorbed by charcoal when in presence of helium, it was decided to test the original gas for argon. A sample was absorbed in charcoal, most of the helium and neon pumped off, and the residue sparked with oxygen to remove the nitrogen. No argon lines could be seen in the spectrum of the remaining gas when observed with the ordinary discharge from an induction coil, but on inserting a Leyden jar and an air-gap into the circuit, a few blue lines became visible. As 0.06 per cent. of argon can be detected in helium with the ordinary discharge (Collie and Ramsay, *loc. cit.*), and the quantity visible in neon probably does not differ greatly, the total amount of argon in the original gas would appear to be small, although it is possible that argon is not easy to detect visually in presence of neon, owing to the similarity of the two spectra, and the great brilliancy of the latter. However, to guard against the possibility of contamination by this gas, the last few c.c. of neon pumped off were always kept separate, and not added to the main quantity.

Hydrogen is easily detected in presence of helium and neon by means of the spectroscope, the most favourable pressure being about 100 mm. The test is, however, almost too sensitive, for it is exceedingly difficult to obtain a sample of gas which does not show

the blue F line owing to traces of moisture, unless the gas is passed from a charcoal bulb straight into a vacuum tube, which has previously been thoroughly heated. 0.001 per cent. of hydrogen is readily detected in helium (Collie and Ramsay, *loc. cit.*), and still less is probably visible in neon, since it is much more difficult to obtain neon showing no hydrogen lines than it is helium. Since 0.01 per cent. would alter the density by less than 1 part in 10,000, the hydrogen spectrum would certainly be quite bright if the quantity present were sufficient to affect the results appreciably. Actually, in all samples used for density determinations, the red C line was always absent, and the blue F line, if visible, only very faint.

It will thus be seen that the detection and elimination of the above-mentioned impurities is a comparatively simple matter, but the case of the remaining impurity, helium, is quite different. Not only is the separation of neon and helium difficult, but it was found quite impossible to detect helium in the mixture spectroscopically even when a considerable quantity was present, although every effort was made to obtain a suitable test. The one finally adopted was an observation of the yellow line D_3 at low pressures. This line (λ 5876) is close to the bright neon line λ 5882, which, in turn, is next to the brightest neon line, λ 5853. The two former lines are just separable with a small spectroscope, with the result that if sufficient helium be present, the line λ 5882 appears double, the difference being very clearly marked. The green helium line λ 5016 does not appear to show as readily as the yellow one, and is, moreover, not so easy to identify.

As previously mentioned, the control of the purity of the gas in the final fractionations was made by means of density determinations, and the values obtained are given on p. 815 in the table of fractionations. It will be seen that fraction 17 consisted of fairly pure gas, and, indeed, its density was greater than that previously found for neon by Ramsay and Travers, namely, 0.891 (*Phil. Trans.*, 1901, **197**, 47). As, however, this did not exclude a still higher figure, fractions 14, 20, 16, and 17 were mixed, making in all rather more than two litres of gas. This was divided into six fractions, the middle four being approximately 400 c.c. each. The densities of these were determined, and it was found that the difference between 24 and 25 was very slight. Consequently they were mixed, absorbed in charcoal, and refractionated; 250 c.c. were pumped off, and the density of the next 400 c.c. taken. This was only slightly higher than before. Now it will be observed that a calculation of the amount of helium present in fractions 21, 22, and 23 (assuming the helium content of fraction 21 to be equal

to that of 22, and the density of pure neon to be not far from 0.9003), shows that the first 700 c.c. contained 63.7 c.c. of helium, and the residual 1350 c.c., only 2.6 c.c., or, in other words, when one-third of the whole quantity of gas had been fractionated off, only 3.9 per cent. of the total helium was left behind. Supposing that a similar state of affairs held good when the mixture of fractions 24 and 25 was being fractionated, it would follow that even if this mixture contained 1 per cent. of helium, the percentage in fraction 28 would be only 0.04, a quantity which would reduce the weight of a litre of pure neon by 0.0004 gram. But the density of fractions 24 and 25 only differed by an amount which corresponds with a difference of 0.1 per cent. of helium content, and therefore, even if the separation was not nearly so perfect as has been assumed, yet the quantity of helium in fraction 28 must have been negligible. However, for the sake of certainty, fractions 28 and 29 were mixed, and the first 110 c.c. removed after condensation in charcoal. The next 400 c.c. were then used for density determinations. Two experiments at room temperature gave respectively 0.9006 and 0.9005 gram as the weight of one litre, and a third at 0° the value 0.9002. Six weeks elapsed before any more densities were taken, and in case any leak of air had occurred in the interval, the gas was allowed to stand in contact with charcoal at the temperature of liquid air for some hours, and then pumped off. Two determinations at 0° both gave the figure 0.8997. The difference of this value from the preceding seemed to be beyond the limit of experimental error, and an effort was made to find out the reason for the change. In the interval between the two series, the volume of the bulb and the Rayleigh correction had been redetermined, and the bulb consequently filled with water. In case this might in some way have affected the results, a test experiment was made by filling the bulb with pure oxygen at 0°. This gas was prepared from potassium permanganate, and purified by passage over soda-lime, phosphoric oxide, and subsequent liquefaction, and the resulting density 1.4287 corresponds with Lord Rayleigh's value, 1.4290, to one part in 5000, that is to say, within the limit of experimental error, so that it seemed likely that the alteration was due to a change in the composition of the gas. A determination was then made with the same sample at room temperature, and the value 0.9001 obtained.

In order to eliminate any possible contamination with helium or hydrogen, fractions 30, 31, and 32 were mixed and passed over red-hot copper oxide for four hours. The gas was next absorbed in charcoal, and about 80 c.c. drawn off. The density of the residue

was determined, first at room temperature, and then twice in ice, the results being respectively 0·9001, 0·9002, and 0·8998.

It will thus be seen that the values found for the weight of a litre of gas varied from 0·9006 to 0·8997, a difference of one part in 1000. This is certainly greater than would be expected from the apparent accuracy of all the measurements and the agreement between the values for the density of the same sample, and so it seems probable that the variation is due to the presence of impurities in the gas. To produce a change of 0·0010 in the density, the presence of 1·1 c.c. of nitrogen, 0·55 c.c. of helium, or 0·50 c.c. of hydrogen in 400 c.c. would be required. Such a quantity of hydrogen or nitrogen would be at once visible spectroscopically, and, moreover, it is difficult to see how contamination with hydrogen could occur. The greatest care was taken to keep all helium or neon containing helium away from the pure neon, and the charcoal was always well heated before introducing the gas, but it is, of course, possible that a mistake was made. Contamination by helium during the interval between the two series of experiments would certainly account for the sudden fall in density, but in this case the refractionation should have removed at least half the helium, so that the density in the last three determinations should have risen more than it did.

Unfortunately, time did not allow a further long series of experiments, and as the variation was so considerable, it was thought unnecessary to make a series of comparative determinations with oxygen, for the slight constant error which might have been detected in this way would certainly be small when compared with the total error.

Below is given an example of the method in which the densities were calculated, the particular experiment being the first recorded in the following table:

June 18th, 1909. Fraction 28.

Weight of bulb empty before experiment	0·01304 gram
" " after " 	0·01306 "
Mean weight of empty bulb corrected for inequality of weights.	0·01309 "
" " " " contraction	0·01298 "
Weight of bulb and gas	0·25888 "
" " corrected for weights	0·25883 "
" gas in the bulb	0·24585 "

As remarked previously, no vacuum correction was applied. The zero change was not appreciable.

Pressure readings.

Upper scale, 69.3 mm., meniscus height	1.0 mm., correction	+0.28 mm.
Lower ,, 29.8 ,, ,, ,,	0.5 ,, ,,	+0.12 ,,

Difference corrected for meniscus heights.....	39.66 mm.
Constant quantity to be added to above	706.17 ,,
Pressure at 18°	745.83 ,,
,, reduced to 0°	743.47 ,,
,, corrected to latitude 45° ($\times 1.000588$) ...	743.91 ,,

Temperature : (a) 18.00° ; (b) 18.06°.

Corrected and reduced to hydrogen scale : (a) 18.00° ; (b) 18.04°.

Mean absolute temperature..... 291.02°

Volume of bulb at 18°..... 297.44 c.c.

Hence the weight of a normal litre is 0.9002 gram.

The following table gives all the results obtained :

	Weight of gas, all corrections made.	Pressure in mm. of Hg at 0°.	Temperature, hydrogen scale.	Weight of normal litre (gram).
Fraction 28.	0.24585	743.9	18.02°	0.9002
	0.24580	747.35	19.50	0.9004
Fraction 32.	0.25031	755.55	17.45	0.9006
	0.25202	757.7	16.26	0.9005
	0.26804	761.1	0.00	0.9002
Fraction 32 (repurified).	0.26779	760.9	0.00	0.8997
	0.26816	761.95	0.00	0.8997
	0.25082	757.9	17.62	0.9001
Fraction 35.	0.25298	763.0	17.06	0.9001
	0.26855	762.6	0.00	0.9002
	0.26933	765.15	0.00	0.8998 *

* See below.

It will be noticed that the values determined at 0° are, in general, smaller than the corresponding ones at a higher temperature, the mean difference being about 0.0003, and it would seem that this difference is due to a wrong assumption having been made as to the coefficient of expansion of the gas, which was taken as 0.003663. Now, it may easily be calculated that in order to bring the two sets of values into agreement, the temperature-coefficient would have to be 0.003645, a figure which differs from the best determined coefficient for hydrogen, namely, 0.003661 by 0.000016. But the coefficient for air determined by the same observer is only greater than that for hydrogen by 0.000009, and hence it seems highly improbable that the values for hydrogen and neon, two gases which have roughly the same critical constants, and similar compressibilities, should differ by an amount which is nearly twice as great as this. It seems more reasonable to ascribe the difference to some constant error in one series of determinations.

The question of purity has already been discussed, and as there seems to be no definite evidence that any one of the samples was

more or less pure than the others, the only course open is to take the general mean of the whole series as the most probable value. The only individual value which is doubtful is the last, for it was found that the weight of the empty bulb was slightly heavier than after the preceding experiment, although the loss in weight after standing in ice was usually about 0.06 milligram. As it is equally probable that the bulb underwent this change in weight (which was permanent, and not due to insufficient exhaustion or removal of grease) before, or after, the gas was weighed in it, it seems only correct to give the experiment half the weight of the others. If this be done, the final mean value obtained is 0.9002. Apart from any theoretical considerations, this is probably correct to 3, or, at the most, 4 units in the last place, and on the low side of the true value.

The Density of Helium.

The available data for the density of helium are very meagre, and the results are discordant, being as follows:

	D. O ₂ =16.	Weight of 1 litre (gram).
Ramsay and Travers *	1.98	0.177
Olszewski †	2.00	0.1785
Schierloh	1.985	0.1773
Kamerlingh Onnes ‡	1.99	0.1775
	2.04	0.182
	2.02	0.180
	2.01	0.179
Mean	2.003	0.1788

* *Phil. Trans.*, 1901, **197**, 47.

† *Ann. Physik*, 1905, [iv], **17**, 997.

‡ *Leyden. Comm.*, 1908, No. 108.

As the apparatus used for the density of neon was capable of giving results of a considerably higher order of accuracy than the preceding, it was decided to make some determinations with helium.

Unfortunately, the author was obliged to leave England when only two experiments had been completed, so that the degree of accuracy is not as great as possible with the apparatus, but nevertheless the figures obtained are given here, since they are probably at least as accurate as those previously published.

The gas used was prepared from thorianite, and was kindly lent me by Sir William Ramsay. It was purified by prolonged passage over copper oxide and charcoal cooled in liquid air in the apparatus previously used for purifying neon, although great care was taken to remove first all trace of the latter gas by repeatedly filling all parts of the apparatus with air and pumping out.

The helium appeared very pure spectroscopically, but as only 0.01 per cent. of nitrogen would raise the density by one unit in

the fourth place of decimals—that is to say, by one part in 1700—it is possible that the error due to the presence of nitrogen was appreciable. To guard against this as far as possible, the gas used in the second experiment was passed into the bulb through a small charcoal tube. It is true that the density diminished slightly after this procedure, but it seems quite possible that the change may have been due to other experimental errors, more especially to those of weighing, for since the total weight of gas was just less than 0.05 gram, this error could not be much less than two parts in 5000. For this reason the determinations were made at atmospheric temperature, so that the bulb could be weighed both before and after each experiment. Actually its weight only varied by 0.01 milligram, but, in spite of this, it does not seem reasonable to suppose that the weighing error on a single determination was less than one part in 2000.

All details and precautions were exactly the same as in the case of neon, and the figures obtained are given below:

Weight of gas, all corrections made (gram).	Pressure in mm. of Hg at 0°.	Temperature, hydrogen scale.	Weight of normal litre (gram).
0.04982	762.25	18.47°	0.17830
0.04945	757.7	18.65	0.17814
Mean			0.1782

This result is not far distant from the mean of the previous values, and should be correct to at least one part in 500.

There is one possible source of error to which my attention has been drawn by Dr. Rudorf, namely, the possibility of surface condensation. Now, to affect the density by one part in 1000, the weight of helium condensed would have to be 0.05 milligram, a quantity which would at normal pressure and temperature occupy 0.3 c.c. The surface of the bulb used was 216 sq. cm., so that the amount of gas condensed per sq. cm. would be 0.0014 c.c. It might at first sight appear possible that this small quantity could be adsorbed, but the recent experiments of Gray and Burt (*Trans.*, 1909, **95**, 1668) on the condensation of hydrogen chloride on glass surfaces render this supposition very unlikely, for it was found by them that 1 sq. cm. of glass adsorbed only 0.00015 c.c. of the gas, that is to say, one-tenth of the above amount. The adsorption of air was far less, and in the case of hydrogen the quantity was almost undetectable. Consequently, it would seem that the adsorption of helium is a negligible factor in density determinations. One point remains to be considered, however, namely, that helium is able to pass through silica, and if this is due to the smallness of the molecules, it might reasonably be expected that the con-

densation on, or diffusion into, glass would be abnormal, but even if this were the case, it seems highly improbable that the abnormality would be so great as to affect the value for the density obtained above.

Analysis of the Gas Mixture.

As before mentioned, two separate cylinders of gas were kindly sent by M. Claude, their contents having been made from the air at two different places. The gas was analysed as accurately as possible for the sake of comparison.

The hydrogen was determined volumetrically by measuring about 7 c.c. of the gas in a constant-volume pipette, mixing with oxygen, exploding, and removing excess of oxygen with phosphorus.

Two methods were adopted for obtaining a pure mixture of neon and helium, the first being to pass the gas over hot copper oxide and a mixture of magnesium and calcium, and the second to absorb the gas in charcoal after a preliminary passage over copper oxide, and then pump off as much as possible. In the latter case a small correction was necessary owing to the fact that not quite all the neon could be so pumped off. Its magnitude was determined by allowing the residue to become warm, taking a small, measured volume, and again absorbing in charcoal. As has been previously mentioned, it was found possible with this small quantity of gas to pump off all the neon, which was then measured. The second method is more tedious, but has to be resorted to when argon is present, for a small trace of argon seriously affects the density.

The results obtained were as follows:

	Cylinder I.	Cylinder II.	M. Claude
Density of gas	0.8631	0.9858	0.985
„ Ne + He, N removed by Mg, Ca	0.7044	—	0.725
„ Ne + He, N „ C	0.6886	0.7321	—
Same corrected for absorbed neon	0.6919	0.7342	—
Percentage of hydrogen	12.6	0.42	0.58*
„ absorbed neon in residue...	1.5	1.2	—

* Determined by weighing amount of water formed.

In the last column are given the results of M. Claude for a sample of gas similar to that in the second cylinder, and it will be seen that his values are fully confirmed.

It is known that oxygen is almost completely absent from the mixture, and so it is possible to calculate the composition from the above data. The ratio of the amount of absorbed neon to the whole volume of gas may be determined by a method of successive approximations, and the remainder of the calculation is quite straightforward, so that it is unnecessary to give it here. The corrected density given in the fourth row is the density which the

pure neon and helium obtained by the charcoal method would have had if there had been no absorption of neon in the charcoal. Now, it will be noticed that, in the case of the gas from the first cylinder, this density (0.6919) is considerably less than the one found by the other method (0.7044). But in order to raise the density to this figure, the percentage of neon in the residues would have to have been 7.3, which was certainly not the case, although the method is not very accurate. The only explanation is that the difference is due to the presence of argon, the total amount necessary being 0.5 per cent. Assuming this amount to be present, and the quantity in the second cylinder to be roughly the same, the complete analyses may be written as follows, the actual amounts of helium and neon being determined from their densities:

	Cylinder I.	Cylinder II.
Helium	12.7	11.7
Neon	31.2	39.3
Hydrogen	12.6	0.4
Argon	0.5	} 48.6
Nitrogen	43.0	

These figures contain two points which are worthy of notice. In the first place, the hydrogen content is very different. The reason for this has been found by M. Claude (*Compt. rend.*, 1909, **148**, 1854) to be due to the fact that part of the air from which the contents of the first cylinder were produced was drawn from a room in which gas-holders were standing. In the second place, the ratio of the quantity of neon to that of helium in the first cylinder is 2.46: 1, and in the second is 3.35: 1. The extreme limits of density for the mixture of helium and neon found by M. Claude in a long series of experiments were 0.685 and 0.74, corresponding with the ratios 2.4: 1 and 3.5: 1. That this difference is not due to experimental error is shown by the fact that in the two more accurate analyses given above, the quantities are in each case near one of the limits.

The comparative nearness of the figures, considering the diversity of experimental conditions, is taken by M. Claude to indicate that, firstly, the proportion of neon to helium in the air is fairly constant, and secondly, the apparatus gave a quantitative yield of rare gas. The mean value is then taken as giving the correct ratio. Looked at from another point of view, however, the second figure is nearly 50 per cent. greater than the first, a difference which is by no means small, and it is difficult to imagine the amounts of helium and neon in the air varying to such an extent. There seems, indeed, to be every reason to suppose that the ratio between the quantities of these gases, at any rate in the same neighbourhood, is of the same order of constancy as the ratio of oxygen to nitrogen.

If this be so, it follows that the differences observed must be due to variations in the working of the machine. Now, the only possible method of loss is by solution of the rare gas in the liquid oxygen and nitrogen. Such loss is almost certainly relatively greater in the case of neon, both because its partial pressure is greater, and because it is nearer its critical point. In this case, the highest value for the ratio of neon to helium will be more correct than the mean value. Again, it is clearly impossible to obtain a larger quantity of rare gas from the atmosphere than that which is present in it, whilst it is very hard to imagine that in any continuous process of partial liquefaction a sudden ebullition of dissolved gas should take place so as to produce an abnormally large yield. Consequently it seems probable that the largest amounts of rare gas obtained from a given quantity of air afford the best estimate of the proportion present.

Now, it will be observed in the contents of cylinder II. the ratio of neon to helium is very high, and, moreover, its contents formed part of an exceptionally large yield, the rate of production being 12 litres an hour from 260,000 litres of air, so that values for the amounts of helium and neon in the air deduced from this analysis should not be very far removed from the true ones, although, even in this case, the results are probably minimum values.

The figures are: Helium, 1 part in 185,000; neon, 1 part in 55,000. They are naturally somewhat higher than the mean values given by M. Claude, and are also greater than those originally obtained by Sir William Ramsay (*Proc. Roy. Soc.*, 1905, *A*, **76**, 111), namely, 1 in 245,300 and 1 in 80,790 respectively, the neon-helium ratio being 3.0: 1. As the method used in this case was absorption by charcoal at -100° , the yield of rare gas would probably not be quantitative, especially as comparatively small quantities were used, although it is difficult to see why as much as 30 per cent. should have been lost. The neon-helium ratio is also probably small, since the gases were actually separated with charcoal at liquid air temperature, and it is very difficult to obtain helium free from neon by this method.

The whole estimation is one of great difficulty, and it only remains to say that it is at least satisfactory that the results obtained by two entirely different methods are, comparatively speaking, so near to one another.

[With FRANK PLAYFAIR BURT.]—In a paper recently published by one of us (Burt, *Trans. Faraday Soc.*, 1910, **6**, Pt. I), an account was given of the determination of the pv isothermals at 0° for helium and neon, it being found that the compressibility coefficients $d(pv)/dp$ between the limits of

pressure investigated, namely, 860 and 150 mm., were constant for both gases. In the case of neon, the coefficient between 0 and 1 atmospheres, that is, $(p_1v_1 - p_0v_0)/(p_1 - p_0)p_0v_0$, the letters having the usual signification, was +0.00105, so that the behaviour of the gas on compression resembles that of hydrogen. For helium the value of pv remained perfectly constant.

With these data, and the values for the density given above, it is possible to obtain a figure representing the atomic weight by means of Berthelot's method.

According to Berthelot, if A is the compressibility coefficient of a gas between 0 and 1 atmospheres, and D its normal density, and if $D(1+A)$ be called the limiting density, then the molecular weights of gases are proportional to their limiting densities.

It follows that if 0.9002 be taken as the density of neon, then its limiting density is 0.9002 $(1 + 0.00105)$ or 0.9011, whilst in the case of helium, the limiting density is coincident with the normal density, that is, 0.1782.

The limiting density of oxygen recently determined by Gray and Burt (*Trans.*, 1909, **95**, 1666), using the same compressibility apparatus, was 1.42762, a figure which is certainly very accurate, the value of the gas-constant R deduced from it being 22.4149.

Adopting this figure for the limiting density of oxygen, since the molecular weight is 32, it follows by simple proportion that the molecular weights of helium and neon are 3.994 and 20.200 respectively.

Summary.

1. A considerable quantity of neon has been isolated in a pure condition, the separation from helium having been effected by means of charcoal cooled to liquid-air temperature.

2. Diffusion through quartz at high temperatures was not found to be a possible way of separating helium and neon, as the medium is slightly permeable to the latter gas.

3. The rate of diffusion of helium through quartz at 1200° was found to be roughly 0.007 c.c. per sq. cm., 1 mm. thick, the pressure difference being 1 atmosphere, a much lower result than that previously obtained by Jaquerod and Perrot.

4. The value obtained for the weight of a normal litre of neon was 0.9002 ± 0.0003 gram.

5. The density of helium was also determined, a normal litre having been found to weigh 0.1782 gram.

6. The quantities of helium and neon in the atmosphere, determined by the analysis of a probably very good sample of the light constituents, were found to be 1 part by volume in 185,000 and 1 in 55,000 respectively, these being minimum values.

7. The molecular weights of helium and neon have been calculated as 3·994 and 20·200 respectively.

In conclusion I should like to express my great indebtedness to M. Claude for his kindness in presenting the materials for this research; to Prof. Collie and Sir William Ramsay for their continued interest and ever-ready assistance; and to Dr. R. W. Gray for much valuable advice.

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LVI.—*The Molecular Weights of Krypton and Xenon.*

By HERBERT EDMESTON WATSON.

THE densities of krypton and xenon have recently been determined by Moore (Trans., 1908, **93**, 2181), the results being considered accurate to about 1 part in 1000. Now it is known that the compressibilities of these gases are considerable, that of xenon being of the same order of magnitude as that of carbon dioxide, for which the compressibility correction to the molecular weight amounts to nearly 1 per cent. The actual compressibilities between 0 and 1 atmospheres have not been measured, but the critical constants are known with some accuracy, and using these it is possible to apply a correction to the atomic weight.

According to Guye (*J. Chim. Phys.*, 1905, **5**, 5), the molecular weight of the more compressible gases is given by the formula $M = RL/(1 + a_0)(1 - b_0)$, L being the weight of a normal litre, and R the gas constant. Also, $a_0 = a(T_c/T)^{3/2}$ and $b_0 = b(2 - T/T_c)(1 - 0.003229P_c/P)$, where a and b are the constants in van der Waals' equation calculated by the ordinary means, $T_c \cdot P_c$ the critical temperature and pressure, and $T \cdot P$ the normal temperature and pressure.

The formula may also be written $M = RL(1 + A)$, where A is the compressibility coefficient between 0 and 1 atmosphere.

Assuming the values for the critical constants given by Ramsay and Travers (*Phil. Trans.*, 1901, **197**, 47), namely, Kr 210·5°, 4124 cm., Xe 287·7°, 4350 cm., a and b may be calculated, and hence A . The values found are -0·00210 and -0·00690 respectively.

It was also found by the same author that for "permanent" gases $M = L(R + 0.0000623T_c)/(1 + a)(1 - b)$, and if this be again written $M = RL(1 + A)$, the value of A for krypton is -0·00228. For argon Guye found the figure -0·00120.

It is interesting to compare these results with those which may be deduced from the actual compressibility measurements of Ramsay and Travers (*loc. cit.*), although as these were only made at pressures greater than 20 metres of mercury, and, moreover, at a temperature of 11.2° , no more than a qualitative significance can be attached to them.

The values given for pv in the cases of argon, krypton, and xenon were carefully re-plotted, and it was observed that in all three cases they appeared to approximate to a straight line at low pressures. For argon and krypton between 20 and 30 metres of mercury, the curves appeared to be quite straight within the limits of experimental error, whilst with xenon, the curvature was very slight. Assuming the lines to be straight, and extrapolating to zero pressure, the values of p_0v_0 obtained were 1825, 1832, and 1825 respectively, whilst from the quantities of gas taken, the calculated p_0v_0 in each case was 1771. However, the curves for argon and krypton will hardly bear extrapolation to this point, and, in fact, if 1771 were the true value, it would follow that the compressibility coefficient of argon at low pressures is positive, whilst the reverse is known to be the case. Now, it is not difficult to see that the compressibility coefficient is largely affected by a comparatively small change in the absolute value of p_0v_0 , so that a small error in measuring the initial volume of gas might alter the former quantity considerably. Details of the amount of gas used for the determinations are not given, but it may be observed that the value of pv for helium, which remained constant between 20 and 30 metres pressure, and is now known to be constant at one atmosphere, is given as 1742, so that errors of the magnitude of 2 per cent. are not to be excluded. It seems therefore justifiable to take the extrapolated values of p_0v_0 in preference to the theoretical one of 1771.

The values of pv at 20 metres pressure for argon, krypton, and xenon are respectively 1784, 1714, and 1492, so that if the compressibility be assumed to remain constant between 20 and 0 metres pressure, the values of A are -0.00085 , -0.00244 , and -0.00694 . These measurements were, however, made at 11.2° , and to correct them to 0° it is necessary, according to Lord Rayleigh (*Zeitsch. physikal. Chem.*, 1905, **52**, 705), to multiply the values of A by the factor

$$(\theta_0^{-1} - 6\theta_0^{-3})/(\theta^{-1} - 6\theta^{-3}),$$

where $\theta_0 = 273/T_c$ and $\theta = (273 + 11.2)/T_c$. If this be done, the values -0.00103 , -0.00288 , and -0.00798 are obtained.

The following table shows the values of $-A \times 10^5$ calculated by the three different methods:

	Ar.	Kr.	Xe.
Compressibility	103	288	798
Guye (1)	84	210	690
„ (2)	81	228	508

Of these, the last figure for xenon may be discarded, as the method used is only applicable to the less compressible gases, and, for the same reason, the last figure for krypton is probably less accurate, although the difference is not great. With argon the compressibility between 1 and 2 atmospheres pressure has been directly determined, although not very accurately, by Lord Rayleigh (*Phil. Trans.*, 1902, A, **198**, 417). The value of A is given as -0.00042 , that of oxygen being -0.00048 . A later determination for oxygen (*Zeitsch. physikal. Chem.*, *loc. cit.*) gave -0.00094 , a figure which corresponds very nearly with the one recently found by Burt and Gray (*Trans.*, 1909, **95**, 1666), namely, -0.000964 . If the ratio between the compressibilities given in the first paper is correct, the compressibility of argon will thus be about -0.00082 , which is almost identical with the calculated value. It may, however, be observed that the mean value calculated for oxygen by these two methods is -0.00085 . This is due to the fact that the gas constant was taken as 22.412, whilst 22.415 is found from experiments with oxygen itself. Consequently the true value for the compressibility of argon is probably -0.00093 , although, in order to calculate the atomic weight with 22.412 as gas constant, the lower value must be used.

Bearing these considerations in mind, it seems that the most probable values for the compressibilities of the three gases are not far from -0.00093 , -0.00215 , and -0.00690 respectively.

The comparative nearness of these figures to those deduced from the compressibility measurements lends considerable confirmation to the accuracy of the methods employed, especially if it be borne in mind that the coefficients at 1 atmosphere pressure are almost certain to be somewhat smaller numerically than at 25.

With regard to the atomic weights of krypton and xenon, the following table gives the mean values, L , for the weight of a normal litre calculated from Moore's figures, and corrected to latitude 45° . The second column shows the pressure at which the gas was measured, and the third the value of RL , R being taken equal to 22.412. The last column gives the values of $RL(1 + A.p/760)$, that is to say, of the molecular weight of the gas:

	L (grams).	p (mm.).	RL .	Mol. wt.
Kr	3.706	475	83.06	82.95
	3.706	772	83.06	82.88
Xe	5.838	446	130.84	130.31
	5.834	521	130.74	130.12

Finally, for the sake of comparison, a table may be given showing the weights of a normal litre measured under 760 mm. pressure, the compressibility coefficients, and the molecular weights of all the inactive gases, although unfortunately there seems to be no obvious connexion between any of these figures:

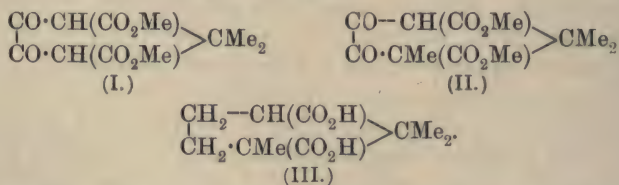
	<i>L</i> (grams).	<i>A</i> × 10 ⁵ .	Mol. wt.
Helium	0·1782	0	3·994
Neon	0·9002	105	20·200
Argon	1·7809	— 93	39·881
Krypton	3·708	— 215	82·92
Xenon	5·851	— 690	130·22

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LVII.—*Komppa's Synthesis of Camphoric Acid.*

By GUSTAVE LOUIS BLANC and JOCELYN FIELD THORPE.

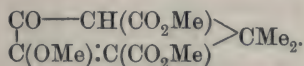
In the year 1903 (*Ber.*, **36**, 4332) Komppa published the preliminary notice of his synthetical preparation of camphoric acid. In carrying out this synthesis, Komppa, in the first instance, improved the yield of methyl diketoapocamphorate (I) obtained in the condensation of methyl oxalate and methyl $\beta\beta$ -dimethylglutarate. From this diketester he then prepared, by the action of sodium methoxide and methyl iodide, a methyl derivative, which he called methyl diketocamphorate, and to which he assigned the formula (II). He finally obtained camphoric acid (III) from this methyl derivative by a process of reduction and hydrolysis:



It was not until last year (*Annalen*, 1909, **368**, 126; **370**, 209) that Komppa published the full experimental details of this important synthesis, and in the last of these papers (*Annalen*, 1909, **370**, 220) he described the preparation of the substance he called methyl diketocamphorate (II), which was the basis of his synthesis. This substance is a well-defined, crystalline compound, melting at 85—88°. It was from the pure crystalline material (*loc. cit.*, p. 221) that Komppa prepared camphoric acid.

In the present paper we show that the substance melting at

85—88° is not, as Komppa supposed, the *C*-methyl derivative corresponding with the formula (II), but is the *O*-methyl ether, having the formula:

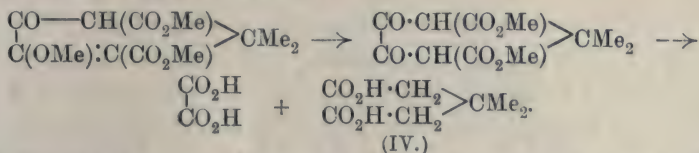


We are therefore of the opinion that Komppa was in error in supposing that he obtained camphoric acid from it on reduction and hydrolysis.

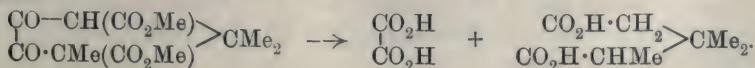
The proof of the methoxy-structure of the substance melting at 85—88° is readily demonstrated in the following way. When a solution of it in aqueous potassium hydroxide containing a large excess of the alkali is kept, a crystalline potassium salt slowly separates. This is the potassium salt of methyl diketo*apo*-camphorate (I), which, we find, possesses the property of being insoluble in strong aqueous potassium hydroxide. When a solution of this potassium salt is acidified, methyl diketo*apo*-camphorate (I) is precipitated in the crystalline form, and under the experimental conditions employed a quantity of the diketo-ester was obtained corresponding with 50 per cent. of the substance melting at 85—88° hydrolysed.

The mother liquors from the precipitated potassium salt were found to give a further small quantity of methyl diketo*apo*-camphorate (I) on being acidified. The filtered solution was therefore treated with permanganate to remove oxalic acid, and on extraction with ether yielded a quantity of dimethylglutaric acid (IV) representing a further 40 per cent. of the substance melting at 85—88° hydrolysed. No trace of $\alpha\beta$ -trimethylglutaric acid could be detected accompanying the $\beta\beta$ -dimethylglutaric acid.

It is, therefore, evident that at least 90 per cent. of the compound Komppa supposed to be methyl diketocamphorate (II) is hydrolysed in accordance with the scheme:



It would be most unusual for a substance of the formula (II) to behave in this manner, for it is a matter of common knowledge that oxalyl derivatives of this type, containing alkyl groups attached to carbon, would be hydrolysed and yield products containing the alkyl groups attached to the same carbon atoms, thus:



Numerous attempts were therefore made to isolate the *C*-methyl derivative isomeric with the above *O*-methyl ether, but without success. Moreover, the neutral oil which remained in the ethereal solution after extracting the methoxy-derivative with sodium carbonate, and which therefore contained the higher alkylated products, was also carefully examined.

This oil, from which no crystalline product could be isolated, was found to yield nothing but oxalic acid and $\beta\beta$ -dimethylglutaric acid on complete hydrolysis, and no trace of $\alpha\beta\beta$ -trimethylglutaric acid could be detected. We are therefore forced to the conclusion that methyl diketoapocamphorate (I), which is, of course, strongly acid in character, does not react in the ketonic form in the presence of sodium methoxide, or, at any rate, that the ketonic phase under these conditions is so short that the quantity of the *C*-methyl derivative formed on methylation with methyl iodide is too small to be detected. It would therefore appear to be hopeless to attempt to prepare camphoric acid from methyl diketoapocamphorate by this means.

EXPERIMENTAL.

The method for preparing methyl diketoapocamphorate recommended by Komppa was carefully followed, and although we were quite unable to obtain the yield mentioned by him, we were able, by using large quantities of material, to prepare sufficient for the purposes of the research. The exact conditions given by him for the preparation of the methyl derivative were also carefully followed, and the same amounts of material were employed. The substance melting at 85—88° was readily obtained, and there can be no question as to its being the same compound as that obtained by Komppa.

The Hydrolysis of the Compound melting at 85—88°.

Ten grams of the substance melting at 85—88° were dissolved in cold aqueous potassium hydroxide, and a large excess of strong alkali was added. The flask was then placed on one side, and shaken from time to time. At the end of one hour a considerable quantity of a heavy, white, crystalline potassium salt had separated. The flask was kept for some time longer until the separation appeared to be complete, when the salt was collected by the aid of the pump and washed with a little alcohol. It was then dissolved in water, the solution acidified, and the precipitated solid filtered. When dried on a porous plate it weighed 4.7 grams, and even in the crude state melted at 112—114°. A small quantity was recrystallised for analysis:

0.1795 gave 0.3582 CO_2 and 0.0953 H_2O . $\text{C}=54.42$; $\text{H}=5.89$.

$\text{C}_{11}\text{H}_{14}\text{O}_6$ requires $\text{C}=54.5$; $\text{H}=5.8$ per cent.

The recrystallised specimen melted at 116° , and possessed the characteristic, crystalline form of methyl diketoapocamphorate. The weight obtained represented 50 per cent. of the substance melting at $85\text{--}88^\circ$ hydrolysed.

The alkaline mother liquors from the potassium salt were then acidified with dilute sulphuric acid, when a small quantity of oil separated which ultimately solidified. This was filtered and dried on a porous plate, when it was found to melt at $100\text{--}105^\circ$. Its weight was not more than 0.2—0.3 gram. The clear solution was then warmed to 50° , and a decinormal solution of permanganate added until a permanent pink colour remained, when it was carefully extracted with ether, and the ethereal solution dried and evaporated. The residue solidified at once, and, after being spread on a porous plate, melted at 100° . A small quantity was recrystallised from hydrochloric acid, yielding the characteristic crystals of $\beta\beta$ -dimethylglutaric acid, melting at 101° :

0.1879 gave 0.3612 CO_2 and 0.1282 H_2O . $\text{C}=52.41$; $\text{H}=7.58$.

$\text{C}_7\text{H}_{12}\text{O}_4$ requires $\text{C}=52.5$; $\text{H}=7.5$ per cent.

The weight of the crude acid obtained was 2.5 grams, corresponding with 40 per cent. of the substance melting at $85\text{--}88^\circ$ hydrolysed. No trace of $\alpha\beta\beta$ -trimethylglutaric acid could be detected in the mother liquors from the recrystallisation of the acid.

THE SORBONNE,
PARIS.

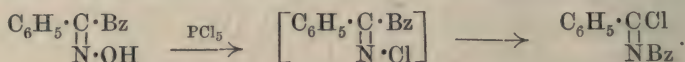
THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

LVIII.—*The Action of Phosphorus Pentachloride on Dibenzamide.*

By ARTHUR WALSH TITHERLEY and ELIZABETH WORRALL.

BENZAMIDE has been shown by the authors (Trans., 1909, **95**, 1143) to react with phosphorus pentachloride, yielding under certain conditions the phosphorus derivative, $\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{POCl}_2$. The behaviour of dibenzamide, as a type of aromatic secondary amide, has now been studied, and it has been shown that no phosphorus derivative is produced, but that a large yield is obtained of α -chloro-*N*-benzoylbenzimidazole, $\text{C}_6\text{H}_5\cdot\text{CCl}\cdot\text{N}\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ (m. p. 87°), which is identical with the compound (m. p. 84°) obtained by Beckmann

(*Annalen*, 1897, **296**, 279) from α -benzilmonoxime by the action of phosphorus pentachloride through the well-known rearrangement:



Preparation of α -Chloro-N-benzoylbenzimidide from Dibenzamide.

An intimate mixture of 5 grams of finely powdered dibenzamide and 7 grams of phosphorus pentachloride was treated with about 40 c.c. of dried chloroform and occasionally shaken. Hydrogen chloride was evolved, and after an hour the action was complete. The resulting chloroform solution was diluted with 50 c.c. of ether and shaken with iced water to remove phosphoryl chloride, the solution dried, and allowed to evaporate. A mass of colourless needles separated in an almost pure condition, melting at 84° , and weighing 4.7 grams (or 80 per cent. of that required by theory). On recrystallisation from light petroleum the α -chloro-N-benzoylbenzimidide was obtained in long, transparent prisms, melting at 87° .

Using ether as a solvent, instead of chloroform, in the preparation, the action is somewhat slower, and a rather smaller yield was obtained:

0.9400, by Kjeldahl's method, required 39.0 c.c. *N*/10-HCl.
N = 5.8.

0.4030 gave 0.2300 AgCl. Cl = 14.13.

$\text{C}_{14}\text{H}_{10}\text{ONCl}$ requires N = 5.75; Cl = 14.57 per cent.

On treatment with aniline in ethereal solution, it gave benzoylphenylbenzamidine, $\text{NPh} \cdot \text{CPh} \cdot \text{NHBz}$, melting after recrystallisation at 143° , and identical with that obtained by Beckmann (*loc. cit.*, m. p. 143°).

The following properties, not recorded by Beckmann, may be described. α -Chloro-N-benzoylbenzimidide is readily soluble in ether, benzene, acetone, or chloroform, moderately so in acetic acid, and rather sparingly so in alcohol. It decomposes on heating by simple fission into benzoyl chloride and benzonitrile. The decomposition is inappreciable at its melting point (87°), and after two and a-half hours only a slight odour of benzoyl chloride is perceptible. At higher temperatures the velocity of decomposition increases rapidly, and was measured by distilling off the benzoyl chloride and benzonitrile in a vacuum at intervals and noting the loss in weight. Precautions had to be taken to exclude traces of moisture, which leads to the formation of dibenzamide. It was found that at 100° 68 per cent. is decomposed in three hours, whilst at 130° 84 per cent. is decomposed in thirty minutes, practically complete decomposition being effected in three hours. The decomposition is not

reversible, and this was confirmed by heating molecular proportions of benzoyl chloride and benzonitrile for several hours at 100° ; no α -chloro-*N*-benzoylbenzimidide was produced. α -Chloro-*N*-benzoylbenzimidide is practically unaffected by contact with cold water or aqueous alkalis for a short time. On boiling with water, it is decomposed into benzonitrile and benzoic acid, the action apparently being preceded by fission. It is surprising that dibenzamide, which might be expected, is not produced, although it is stable under the conditions of the reaction. Beckmann, however, noted that α -chloro-*N*-benzoylbenzimidide slowly decomposes on keeping, giving dibenzamide and benzoic acid, especially when it is not quite pure. The authors have confirmed this observation, and have shown that even after careful purification the originally transparent crystals become gradually opaque, and after four or five weeks are almost completely transformed into dibenzamide, benzoic acid, and benzonitrile through the action of atmospheric moisture or ordinary water. By heating on the water-bath at about 95° in a shallow vessel exposed to air, the transformation is complete in twenty-four hours; the clear liquid slowly crystallises, and eventually completely solidifies. The yield of dibenzamide, which melted after recrystallising from alcohol at 147° , was about 60 per cent., the remainder being accounted for by simultaneous fission which takes place, giving benzoyl chloride and benzonitrile, which pass off. Again dibenzamide results, in a good yield, when α -chloro-*N*-benzoylbenzimidide is decomposed by 98 per cent. sulphuric acid; hydrogen chloride is disengaged, and dibenzamide is precipitated on subsequent dilution of the acid with water.

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LIX.—*A Method for the Approximate Estimation of Small Quantities of Lead.*

By A. G. VERNON HARCOURT.

MANY years ago the author, having to deal with the estimation of the amount of sulphur in coal-gas, proposed the use of an apparatus in which the gas, containing a small proportion of hydrogen sulphide, was drawn through a solution of a lead salt. As the gas passed in a stream of small bubbles through the lead solution, the colour of the solution gradually darkened. By the

side of the glass cylinder which held the liquid there stood, on a white surface and with a white background, a similar cylinder holding another brown liquid, the colour of which matched that of the lead solution when the latter had combined with a known amount of sulphur. The stopcock of the aspirator was turned off as soon as the depth of colour was the same in the two tubes, and the volume of gas which had contained the known amount of sulphur was found by measuring the water drawn from the aspirator.

To obtain a clear brown liquid and not a precipitate, there was used a solution of lead in an excess of sodium hydroxide, to which was added a solution of cane sugar. For the standard colour, lead sulphide could not be used, since its colour gradually fades by the action of light; but the colour can be matched by mixing in due proportions solutions of the sulphates of copper, cobalt, and ferric iron, and the colour of this mixture when sealed up in a glass cylinder remains unchanged.

Having recently to deal, as a member of a Home Office Committee, with glazes containing lead, and with the minute amounts of lead which rise and are breathed in as dust by workers at potteries, it occurred to me that the process above described might be inverted, and thus turned to account, by using hydrogen sulphide as the reagent for estimating lead under similar conditions.

If the lead compound is in solution, as in the case of soft water which has been in contact with lead, or can readily be separated from other substances, with which it is associated, by solution in an acid or an alkali, the estimation is made in the following manner. A few particles of lead nitrate or chloride are dissolved in water in such proportions that there will be one centigram of lead, or of lead oxide (whichever system is preferred), in a litre. A dozen thin glass cylinders must be procured, each 15 cm. in height and 2.2 cm. in external diameter with a line etched round it marking the level of a capacity of 50 c.c. Into one of these is brought 25 c.cm. of the standard solution of lead, a few drops of dilute nitric or hydrochloric acid, a similar quantity of a concentrated solution of sodium acetate (with hydrochloric acid the liquid becomes turbid unless sodium acetate is added first), 10 c.c. of a clear syrup, half sugar and half water, 0.5 c.c. of a solution of hydrogen sulphide, and, lastly, water up to the 50 c.c. mark. For mixing these liquids a good form of stirrer is a plunger of a diameter slightly less than that of the tube, made by blowing a bulb at the end of a piece of thin glass tubing and flattening it to a hemisphere. Strong agitation of the liquid must be avoided, for it may cause precipitation of lead sulphide; two or three passes

of the plunger up and down after the addition of each fresh ingredient make a perfect mixture. The result in this case will be a clear pale brown liquid, which will remain unchanged for at least half an hour if only exposed to full daylight when its colour is being compared.

To prepare the standards, the solutions of the three sulphates are mixed in a flask or bottle of about half a litre capacity, adding water when the colour, otherwise similar to that of the lead sulphide, is too deep. The comparison is made by filling one of the tubes from the flask up to the line and placing this tube and that with lead side by side on a sheet of white paper, then pouring back and refilling and again comparing, after each addition of one or other of the blue, red, or orange liquids. The ferric sulphate is conveniently prepared by weighing out and dissolving ferrous sulphate, adding the requisite quantity of sulphuric acid, and dropping nitric acid little by little into the warm liquid until no darkening is seen, then heating and shaking until the nitric oxide has gone. It is important to have no large excess of acid, which seems in course of years to act on the glass and form a white deposit. The colour of ferric chloride varies more with temperature than that of ferric sulphate, and therefore in making a standard colour it is better to use the sulphate. Before drawing out and sealing the top of the tube, it is well to ask the judgment of several pairs of eyes on the agreement, in colour and in depth of colour, between the lead and the standard liquids, and also to repeat the preparation of the former and make a second comparison.

Eight other standard tubes are to be charged in the same manner, matching respectively liquids made up with 19, 14, 10, 7, 5, 3, 1.5, 0.5 c.c. of the solution of lead. From the coloured liquid made up to match the sulphide produced by 25 c.c., corresponding with 0.00025 gram of lead, or lead oxide, the liquids to match the smaller proportions can be made nearly, but not quite, by simple dilution. The comparison must be repeated in every case, and by small additions of water, or of the darker liquid, or of one or other of its ingredients, the match is to be made as perfect as possible. When the quantities of the standard lead solution are smaller, the tube is to be filled up with water nearly to the line before hydrogen sulphide is added. The set of nine standards thus made up fit neatly into a small box; they will last for any time, and serve for any number of estimations, each occupying only a few minutes, and for all cases in which a very small quantity of lead has to be estimated, and no other metal precipitable in an acid solution by hydrogen sulphide is present.

To make the estimation, an aliquot part of the lead solution,

chosen according to its probable concentration, is treated as above. If the colour is paler than that caused by half a centimilligram of lead, more of the liquid must be taken, if necessary after evaporation and fresh measurement; if the liquid is darker than that corresponding with 25 centimilligrams, less must be taken, if necessary after dilution. On either side of the lead tube are placed, on a large sheet of white paper, if possible near a window looking to the north, the two standards which it most resembles. Suppose these to be 10 and 7. If it matches one of these, that number is taken. If it falls between the two, judge to which it is nearer. In one case 9, in the other 8, is the number chosen. But an alternative and probably the better form of stating the result is, that the amount of lead extracted under specified conditions from a weighed sample of dust or glaze or frit is not more than $10 v/v'$ nor less than $7 v/v'$ centimilligrams, where v is the total volume of the extract, and v' the volume taken for testing.

Where grams or decigrams of a sample are obtainable and sufficient time and unfailing care can be bestowed, and where a result that may be trusted to within one or two per cent. is necessary, a determination by weight is best. But where the samples available, or the proportion of lead extractable from the samples, are centigrams or milligrams only, the probable error of a determination by weight becomes very great. In this case a rapid method, which, while giving only approximate results, is quite trustworthy within its limits, seems preferable.

A few incidental observations may be added. Such dilute solutions of lead as are here dealt with are not coloured on addition of hydrogen sulphide in presence of even a very small proportion, such as one in two or three hundred, of nitric acid. When sodium acetate is added, the brown colour appears. Hydrogen sulphide dissolved in boiled-out water, transferred to a burette, and covered with a few drops of olive oil, will remain clear for weeks. A solution of sugar becomes turbid on standing; the turbidity passes through a filter. Testings cannot be made if all the solutions used are not clear, nor if sulphur is formed in the liquid; a scarcely perceptible opalescence affects the colour and the depth of colour, and makes the comparison difficult. A few drops of carbon disulphide kept in the flask in which the sugar is dissolved seem to help in preventing turbidity.

The comparison of the lead and standard tubes is best made, where the amount of lead is 10 centimilligrams or under, by observing only the appearance of the disk forming the upper surface of the liquid; where the amounts are larger the disk is almost too dark for comparative observation, and the comparison is helped by

also looking from a little distance off through the sides of the cylinders. Standards made up in daylight no longer resemble the lead sulphide coloration by ordinary gas light or that of the electric glow lamp, but in the light of a good incandescent mantle the colours agree as in daylight.

The set of tubes here described, with others similarly made up of a darker shade, could also be used for determining the amount of sulphur in a sample of iron or steel, by a method shown to the British Association and published in the *Chemical News* in the year 1879.

Part of the experimental work on which the above method and observations rest was done in the laboratory of Pathological Chemistry at University College, London, by permission of Dr. Vaughan Harley, and part in the laboratory of Christ Church, Oxford, by permission and with the kind assistance of Dr. H. B. Baker.

LX.—*The Interaction of Hydrogen and Chlorine. The Nature of Photochemical Inhibition.*

By DAVID LEONARD CHAPMAN and PATRICK SARSFIELD MACMAHON.

It has been already remarked (Trans., 1909, **95**, 1717) that the gases which are known to retard or prevent the photochemical interaction of hydrogen and chlorine are, without exception, easily reducible substances, and it has been inferred that probably the retarding effect is indirectly due to the reduction of the inhibitor by hydrogen or hydrogen chloride.

The ground for the above conclusion concerning inhibitors was the following ascertained facts. Oxygen, nitrogen chloride, and the gas formed by the action of moist chlorine or nitric oxide (nitrogen peroxide or nitrosyl chloride) acted as inhibitors, whilst carbon dioxide, nitrogen, and nitrous oxide were mere diluents. That nitrous oxide should appear amongst the list of diluents is not contrary to expectation, since this gas is, in most circumstances, chemically inert. Oxygen is by far the most feeble inhibitor, and it is also the least chemically active.* Nitrogen chloride and

* As yet, no disappearance of oxygen from an illuminated mixture of hydrogen and chlorine containing it has been detected; but sufficiently forcible a priori considerations can be adduced in support of the assumption that oxygen will slowly react with hydrogen chloride in the presence of chlorine under the influence of light.

It is possible that a complete theory must include electrical conceptions; but so far our attempts to formulate an electrochemical hypothesis have only involved us in a maze of assumptions and speculations apparently incapable of experimental verification. We have therefore adopted, for the present, a working hypothesis, in which the photochemical character of the phenomenon is emphasised. According to this hypothesis the energy which enters the system through the chlorine molecules is distributed between the various constituents of the system. If no inhibitor is present an extremely small amount of the transformed energy is sufficient to bring about the union of finite quantities of hydrogen and chlorine. But if an inhibitor is present, the efficient energy is partly (in most cases almost entirely) employed in promoting its reduction, and a considerable amount of energy is degraded in bringing about the reduction of small quantities of the inhibitor.* The assumption that a comparatively large amount of energy is required to reduce a small quantity of inhibitor is in some cases capable of experimental verification. The experiments undertaken with this object in view do not naturally fall within the scope of this paper, and they therefore will be reserved for a future communication.

EXPERIMENTAL.

The Inhibitory Effect of Ozone.

In the following experiments we have measured the effect of ozone on the rate of combination of the electrolytic gases under similar experimental conditions to those which obtained in our work on the retarding influence of nitric oxide on the velocity of formation of hydrogen chloride.

Ozone has entirely fulfilled our expectations in acting similarly to nitric oxide, and its behaviour taken with that of oxygen has afforded an interesting comparison. The measure of its inhibitory power differs very little from that of nitric oxide. In so far as there is a difference, ozone is the more powerful inhibitor.

The apparatus was the same as that employed in the previous investigation on nitric oxide. As ozonised oxygen frequently contains minute quantities of the oxides of nitrogen derived from a trace of nitrogen contained in the oxygen from which it is prepared, the gas from the ozoniser was passed through a wash-bottle containing concentrated sulphuric acid, which is a very effective absorbent of nitrogen peroxide, and was then allowed to

* It will be observed that the hypothesis does not preclude the possibility of an oxidisable gas acting as an inhibitor provided that it satisfies the necessary conditions.

bubble slowly through water, acidified with sulphuric acid, into a small gas-holder. When the water was saturated with ozone, the supply of gas was shut off, and the ozone kept in the gas-holder for periods varying from two to ten days. By observing these precautions it was hoped that nitrogen peroxide would be completely removed. It may here be observed that potassium hydroxide solution cannot be employed to absorb the oxides of nitrogen, since ozone is extremely unstable in the presence of alkalis.

The measure of ozonised oxygen added amounted to about $1/300$ th of the total volume of gas in the insolation vessel. In all the experiments the source of light was a 25 c.p. electric lamp, as the more constant Hefner lamp was found to be too feeble for the investigation of the inhibitory effects.

In the preliminary experiment one measure of ozonised oxygen was added to the sensitive mixture in the actinometer in each case. Experiments were performed in which the original sensitiveness of the electrolytic gas varied from 6 to 21 cm. per minute with the lamp placed at a distance of one metre from the insolation vessel. The exposure was half an hour commencing immediately after the addition of the ozone, and in no case could any movement of the index be detected during that period. •

In a second series of experiments concentrated sulphuric acid was substituted for the acidified water in the gas-holder. The ozonised oxygen was retained in the gas-holder for ten days before use. Some of the experiments are recorded in detail below:

(a) The sensitiveness of the gas was 2.1 cm. per minute with the lamp at a distance of one metre. After the addition of a measure of ozone the insolation vessel was exposed for one hour to the light of the lamp placed at a distance of 30 cm. No movement of the index could be detected. The mixture was then left in the dark for ten hours. On re-exposure to light, combination started immediately, the maximum rate of union of 1 cm. of the index per minute being rapidly attained. Ozone therefore disappears from the gaseous mixture in the dark.

(b) The sensitiveness of the gas was 5 cm. of the index per minute, the lamp being at a distance of one metre from the insolation vessel. The distance of the lamp from the insolation vessel was then reduced to 20 cm. A measure of ozone was added to the electrolytic gas in the dark, and the mixture exposed to the rays of the lamp. At the end of one hour and twenty minutes the index liquid began to move very slowly, and at the end of one hour and thirty minutes was moving at the rate of 3 mm. per minute.

(c) A measure of ozone was added to the insolation vessel, which

was then allowed to remain in the dark for eighteen hours. Subsequent exposure to light proved that the ozone had completely disappeared; there was no "induction period."

(d) After the addition of a measure of ozone the mixture was allowed to remain in the dark for an hour and forty-five minutes only, before being exposed to the light of the lamp at a distance of 20 cm. The length of the "induction period" was between twenty and thirty minutes.

Acidified water was again substituted for concentrated sulphuric acid in the small gas-holder, and the experiments were repeated. The readings obtained in one experiment are recorded *in extenso*.

The original rate of combination of the chlorine and hydrogen was 4.5 cm. of the index per minute, with the lamp at a distance of 100 cm. from the insolation vessel. This distance was now decreased to 20 cm., and ozone added:

Time of exposure in minutes.	Scale reading, in cm.	Rate of combination, in cm.
51	1.50	0.00
54	1.70	0.20
57	2.00	0.30
60	2.35	0.35
63	2.60	0.25
66	2.90	0.30
69	3.30	0.40
72	3.70	0.40
75	4.15	0.45
99	14.15	1.25

The rate of combination then increased rapidly to 5 cm. per minute. With the lamp at the original distance of 100 cm. from the insolation vessel, the maximum rate of combination was 9 mm. per minute.

It was finally necessary to show that the means adopted to remove traces of the oxides of nitrogen from the ozonised oxygen were sufficiently effective. To do this oxygen previously mixed with 5 per cent. of nitric oxide was bubbled through water into the small gas-holder, and allowed to remain in the presence of water for one day. Sensitive electrolytic gas in the insolation vessel, mixed with two measures of this oxygen, failed to exhibit any sign of an "induction period." The inhibitory agent in the above experiments was therefore ozone.

The Inhibitory Effect of Chlorine Dioxide.—The chlorine dioxide was prepared from potassium chlorate and concentrated sulphuric acid. The potassium chlorate was recrystallised from boiling water. In the later experiments potassium chlorate, crystallised from an aqueous solution which had been saturated with chlorine and boiled for many hours in a flask provided with a ground-in reflux condenser, was used. In the same experiments the sulphuric

acid was several times saturated with chlorine and heated before being used. The chlorine dioxide was prepared by adding in small quantities well dried and finely powdered potassium chlorate to concentrated sulphuric acid contained in a small bulb surrounded by a freezing mixture. The bulb, while still surrounded by the freezing mixture, was connected by means of a ground glass joint with that part of the apparatus designed for adding a measured quantity of gas to the actinometer. The temperature of the bulb was then raised to about 30° , and chlorine dioxide was evolved. The results of a few experiments are recorded below.

A sufficient volume of chlorine dioxide was mixed with the electrolytic gas in the insolation vessel to give a mixture containing one volume of chlorine dioxide to fifty volumes of electrolytic gas. For intervals amounting in all to over seventy hours and extending over five days, the mixture was exposed to the rays of a 25 c.p. tantalum glow lamp placed as near as possible to the glass window of the tank in which the insolation vessel was immersed. At the end of the seventy hours' exposure to light, the gas began to combine slowly under the influence of the rays from the glow lamp. The activity of the mixture gradually increased, and ultimately attained a maximum value equal to about $1/40$ th of the original sensitiveness of electrolytic gas.

In another experiment one measure of chlorine dioxide only was added to the electrolytic gas in the insolation vessel. The original sensitiveness of the electrolytic gas corresponded with a movement of 36 cm. of the index per minute with the 25 c.p. carbon filament lamp at a mean distance of 20 cm. from the insolation vessel. For four days there was no sign of combination, the total exposure to light during this period amounting to about fifty hours. The tantalum lamp was then placed as near to the insolation vessel as the tank permitted, and under these conditions slow combination was noted. The rate of interaction of the chlorine and hydrogen increased at first very slowly, and then more rapidly up to a maximum of about 3 cm. per minute.

An interesting result, which we are unable at present to explain, is obtained when very small quantities of chlorine dioxide are mixed with the electrolytic gas. With such a mixture interaction of the chlorine and hydrogen proceeds at a slow and uniform rate for an hour or more, and then there is a sudden increase in the velocity of combination.

The Influence of Chlorine Monoxide.—Chlorine monoxide was found to have no inhibiting effect on the union of chlorine and hydrogen. In several preliminary experiments chlorine was passed through a glass tube packed with mercuric oxide, and about 2 c.c.

of the resulting gas were passed into the insolation vessel. The mixture thus obtained did not exhibit the phenomenon of induction, but it was found to be four times less sensitive than the original gas. The fall in sensitiveness was almost certainly due to some oxygen derived from the partial decomposition of the chlorine monoxide.

In the next experiment the chlorine monoxide was liquefied in order to free it from oxygen, and 2 c.c. of the vapour were driven into the insolation vessel. On exposure of the resulting mixture to light, there was no induction period, and in this case only a slight retardation. After the liquid chlorine monoxide had been evaporating some time and all the oxygen had been driven out of the bulb which contained the chlorine monoxide, a further amount of vapour was added; there was no induction period, and no further retardation. Finally, a large volume of chlorine monoxide (about 25 per cent. of the volume of the insolation vessel) was added. There was neither an "induction period" nor a measurable decrease in sensitiveness. Chlorine monoxide has therefore no effect on the rate of combination of hydrogen and chlorine in light.

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LXI.—*The Action of Water of Crystallisation on Calcium Carbide.*

By IRVINE MASSON.

IN a note read before the Society of Chemical Industry of Victoria in 1900, H. A. Danne was the first to describe the use of calcium carbide as a means of determining moisture. The method was applied chiefly to the hygroscopic water in various organic substances, but was also used for examination of moisture in saline compounds. Briefly, it consisted in driving off the water into calcium carbide by heating in a glycerol bath, and collecting and measuring the evolved acetylene over water previously saturated with the gas. Danne states that there is a marked interval between the evolution of gas due to hygroscopic and that due to combined water.

Some years later P. V. Dupré (*Analyst*, 1906, **31**, 213) described a similar method, specially applicable to cordite and other substances which evolve water vapour together with other volatile

matters when heated. In this method, as in the first, the water was evaporated into carbide by heating in a bath of boiling water, and the gas evolved was measured in a nitrometer over brine. It is here noted that combined water in hydrated salts is driven off at a slower rate than is hygroscopic water.

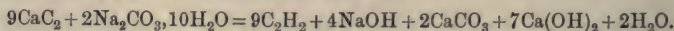
Recently an Australian Conference on moisture in wool has adopted a considerable modification of Danne's method for determining the hygroscopic state of wool. In this it is found sufficient to shake the wool clippings with a large excess of powdered calcium carbide, the acetylene being determined by measurement either of volume at constant pressure or of pressure at constant volume. No heating is required.

In this connexion it seemed of interest to know whether carbide in direct contact has any action on the combined water of salts. The only references to this subject are by Dupré (*Analyst*, 1905, **30**, 266) and by Turner (*Amer. Chem. J.*, 1907, **37**, 106). The former, in a paper on the composition and stability of ammonium oxalate crystals, states that when this salt was mixed with carbide and the mixture placed in a bath at 70°, acetylene was quickly evolved, the action being complete in about half a minute. The volume of acetylene corresponded roughly with the amount of water of crystallisation of the salt. Dupré then abandoned the process of mixing, and used that described in his later paper already referred to. Turner, in a paper on another subject, states incidentally that sodium carbonate crystals are being used commercially in place of water for generation of acetylene in order to avoid violent action.*

The following investigation was undertaken to ascertain whether crystalline hydrates in general react when intimately mixed with excess of calcium carbide; whether they do so without external application of heat; and to what extent the actions in the cold or on heating are complete.

On mixing excess of calcium carbide with a crystalline hydrate, both finely powdered, in an apparatus suitable for collecting and

* This statement evidently refers to the Atkins Dry Process, an account of which (*Engineering*, 1906, **81**, 261) has been brought to my notice since writing this paper. In this account, the following equation is given for the action which occurs on mixing the charge of carbide with soda crystals:



No experimental support for this equation is quoted. My own results, as shown in the sequel, prove that (1) all the combined water of the soda crystals is used to produce acetylene; (2) no chemical action between the dry solid products takes place (see ammonium salts, oxalic acid, and acid phosphates), and, therefore, the formation of sodium hydroxide and calcium carbonate represented in the above equation probably occurred, if at all, during subsequent examination of the residual products.

measuring the gas evolved, action ensues, more or less energetic according to the salt employed. Thus with sodium carbonate decahydrate and a few others of the salts examined, generation of acetylene occurs at once with evolution of heat and is complete within a few seconds, the salt being entirely dehydrated. This action furnishes an instructive lecture experiment.

With other salts the action is comparatively slow at the ordinary temperature, but proceeds swiftly at slightly higher ones; whilst with others again, action is slow and steady even at 170° to 180° . Higher temperatures have not been tried.

That a salt which is but slowly dehydrated in the desiccator or even in the oven should be completely dehydrated in a few seconds by contact with powdered calcium carbide is somewhat surprising, and the whole appearance of the action might well lead to the supposition that the two dry solids concerned react directly with each other. It is questionable, however, whether interaction of dry solids, giving dry products, ever occurs unless perhaps under very intense pressure, and the cause is evidently rather to be sought for in the action of the closely adjacent carbide on water vapour emitted by the hydrate, which thus undergoes loss of water without the counteracting effect of return of water molecules to its surface, such as must occur to some extent when the salt is dehydrated in the desiccator or in the oven.

With hydrates of high vapour-tension, the action is rapid and hence generates considerable heat, causing automatic acceleration; whilst with those of low vapour-tension, action is slow and the heat generated is dissipated by the usual cooling processes, no noticeable rise of temperature occurring.

With a given salt, the conditions controlling the rate of evolution of acetylene are, first, extent of surface of contact with carbide, and, secondly, the temperature at which the reaction is taking place, which may be either that produced by artificial heating or the result of the heat of the reaction itself. The reaction thus differs from one occurring in solution, the velocity of which is governed only by the laws of action in homogeneous systems. The degree of sub-division was found, however, to exert less influence on the velocity than would be anticipated, and did not affect the ultimate result.

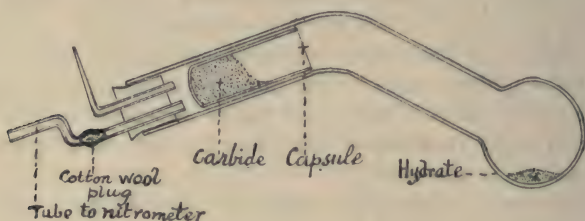
EXPERIMENTAL.

The apparatus used was simple. The reaction-tube consisted of a stout-walled glass test-tube of about 35 c.c. capacity with a bulb at the closed end and bent in the middle through an angle of about 45° . A glass capsule, of such a size that it fitted easily inside the reaction-tube but could not pass the bend in the middle, served

to hold the charge of carbide. The reaction-tube was closed with a rubber stopper bearing two exit tubes, one drawn out to a point which could be sealed when required, the other containing a small plug of cotton wool as a filter for carbide dust and serving as an exit for the gas (see figure).

The acetylene was collected in a nitrometer over mercury. Collection over water or aqueous liquids was rejected on account of errors due to solubility. The pressure of the gas as it entered the nitrometer was kept constant as far as possible by alteration of the level of the mercury reservoir. The connecting tube leading to the nitrometer was of glass, with two or three short joints of thick-walled rubber tubing to give flexibility and allow the reaction-tube to be shaken. The extent of rubber traversed by the gas was reduced to a minimum, as the acetylene was to a small extent absorbed by it.

The carbide used was a commercial brand of finely powdered



material. The hydrates experimented with were pure commercial specimens and, where necessary, were recrystallised.

Good crystals were selected and crushed as finely as possible without undue exposure, and the sample to be used was weighed into the reaction-tube. The quantity taken was that calculated to give a volume of gas suitable for measurement, a preliminary test being made when necessary. Three grams of carbide (a large excess) were placed in the capsule before referred to, which was then introduced into the reaction-tube, tilted at such an angle that no premature mixing of carbide and hydrate could occur. The rubber stopper was then fitted in. The levels of mercury in the nitrometer and reservoir were equalised, and the drawn-out tube in the stopper of the reaction-tube was sealed when the latter had recovered from the warmth of handling. The temperature of the air and the height of the barometer having been read, the carbide and hydrate were mixed by tilting the reaction-tube so that the carbide fell out of its capsule, which was caught in the bend, on to the hydrate, with which it was well shaken. The gas evolved was measured some time after the reaction was over in

order to obviate disturbances due to the heat of the reaction. If by any change in the laboratory temperature or the barometric pressure the amount of gas contained in the reaction and connecting tubes had altered, the necessary small correction was introduced.

If it was desired to heat the mixture, the lower part of the reaction-tube was immersed in a bath either of water or of sulphuric acid. After heating, one or two hours were allowed to elapse before measuring, as a small amount of acetylene, at most 0.5 c.c., was given out by the rubber stopper on heating, which required time to be re-absorbed. To minimise small errors arising from this absorption, the rubber stopper and connexions were always saturated with the gas before an experiment.

Standardisation.

For this purpose about 0.2 c.c. of distilled water was accurately weighed into the reaction-tube, and the experiment was conducted as described. In the table are given the values obtained for the volume of gas in c.c. at 0° and 760 mm. corresponding with 18.0 milligrams of water, that is, with one millimol. The temperature to which the tube was raised is shown at the head of each column:

Carbide <i>A</i> .	Carbide <i>B</i> .		
Cold.	Cold.	100°.	170°.
10.50	10.30	—	—
10.46	10.54	—	—
10.38	10.36	10.73	—
10.56	10.31	10.71	10.64
10.47	10.40	10.80	—
10.50	10.34	10.72	10.71
—	10.28	10.68	10.68
Mean ... 10.48	10.36	10.73	10.68

As both samples of carbide were used, and as the degree of heating, which seems to affect the value slightly, was an uncertain quantity in many experiments owing to the rise in temperature occasioned by the heat of reaction, a value of 10.5 c.c. per millimol. of water was taken throughout as the working factor, which should give results varying by not more than about 2 per cent. from the true values.

It is interesting to note that Dupré found that 1 c.c. of gas at 0° and 760 mm. corresponds with 1.725 milligrams of water, or 10.45 c.c. corresponds with one millimol. of water. The coincidence is somewhat remarkable, since Dupré's experimental conditions were quite different from those used here.

According to Moissan's well-known equation for the interaction of water and pure calcium carbide, two molecules of water act on

one molecule of carbide, producing one molecule of calcium hydroxide and one molecule of acetylene; hence one millimol. of water should give 11.17 c.c. of gas. It is known, however, that the yield of gas from commercial carbide is less than this, and this result has been attributed to the impurities in the carbide and also to polymerisation of the acetylene. It is possible that the variation is due to the presence of quicklime in the carbide.

Results.

In the tabulation of results, values are given for:

W = milligrams of hydrated salt used;

V = c.c. of gas reduced to 0° and 760 mm.;

$N = \frac{VM}{10.5 W}$ = the number of water-molecules reacting in every molecule of hydrate of molecular weight = M .

At the head of the columns is given the temperature at which the reaction-tube was kept. Unless otherwise mentioned, the action was quickly over at this temperature; but in all cases heating was continued long enough to make certain of the finality of the action, measurements of the gas being made at intervals.

1.—Sodium Carbonate Decahydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$. $M = 286.2$.

W .	Cold.		100°.	
	V .	N .	V .	N .
346.8	125.3	9.85	—	—
330.8	121.0	9.97	124.1	10.23
329.2	120.2	9.95	123.5	10.22
322.2	115.9	9.80	—	—
	Mean.....	9.89		10.22

Ignition of duplicate samples at red heat gave in each case a loss of $10.04\text{H}_2\text{O}$ (calc. 10.00).

In this case, action with carbide is practically over in thirty seconds and, as is seen from the table, dehydration is almost complete without application of heat other than that generated by the reaction.

2.—Sodium Sulphate Decahydrate, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$. $M = 322.2$.

W .	Cold.		100°.	
	V .	N .	V .	N .
354.1	113.9	9.87	117.3	10.17
350.7	112.8	9.87	116.2	10.17
	Mean	9.87		10.17

Ignition of duplicate samples at red heat gave a loss of $10\cdot00\text{H}_2\text{O}$ in each case (calc. $10\cdot00$).

The action on carbide is similar to that of the last salt and, as in that case, shows a slightly low value in the cold and a slightly high value in the hot action. This may perhaps indicate nothing more than a variation in the factor taken as $10\cdot5$, such as occurred even in standardisation.

3.—*Trisodium Orthophosphate Dodecahydrate*, $\text{Na}_3\text{PO}_4\cdot 12\text{H}_2\text{O}$.
 $\text{M} = 380\cdot2$.

W.	Cold.		100°.	
	V.	N.	V.	N.
353·5	107·0	10·96	113·9	11·67
345·4	104·1	10·91	112·0	11·74
	Mean	10·94		11·70

The salt had been recrystallised in a vacuum and dried for three weeks over partly dehydrated crystals of the same salt. Nevertheless, it was evidently somewhat impure, for duplicate samples ignited to constant weight at red heat gave losses of $11\cdot73$ and $11\cdot72\text{H}_2\text{O}$ (calc. $12\cdot00$), in agreement with the results obtained with carbide at 100° . The results at the room temperature suggest the formation of a relatively stable monohydrate, which is known to exist.

4.—*Disodium Hydrogen Orthophosphate Dodecahydrate*,
 $\text{Na}_2\text{HPO}_4\cdot 12\text{H}_2\text{O}$. $\text{M} = 358\cdot2$.

W.	Cold.		100°.	
	V.	N.	V.	N.
322·6	115·2	12·18	—	—
333·2	119·3	12·21	—	—
323·6	115·9	12·22	120·1	12·66
323·2	117·3	12·33	121·7	12·85
305·0	107·6	12·03	112·9	12·63
303·6	109·1	12·26	113·2	12·72
312·1	112·4	12·28	—	—
	Mean	12·22		12·72

The salt used was recrystallised and dried in the same way as the last one. Duplicate conversions into pyrophosphate at red heat gave losses of $12\cdot54$ and $12\cdot56\text{H}_2\text{O}$ (calc. $12\cdot50$).

The carbide action, which is as fast as in the previous cases, evidently renders the salt anhydrous, and may also involve partial removal of the constitutional water of the molecule Na_2HPO_4 ; this it certainly does at 100° . That this conversion into pyrophosphate should go on at so low a temperature is surprising, as

when heated alone sodium phosphate is said not to decompose much below red heat. There are two objections to the suggestion that this might take place indirectly through interaction of the salt Na_2HPO_4 with the calcium hydroxide formed in the first action. First, the mixture is free from traces of moisture, without which, it seems fair to suppose, the action would not proceed; secondly, according to any equation which can be constructed for such an action, the quantity of water set free would be in considerable excess of that found by experiment. It seems, then, that conversion into pyrophosphate takes place in the same way as loss of ordinary water of crystallisation, and that the behaviour of the salt towards carbide is the same as that which would be expressed by formulating the compound as pyrophosphate plus water of crystallisation, that is, $\text{Na}_4\text{P}_2\text{O}_7 \cdot 25\text{H}_2\text{O}$, in which one molecule is rather more stable in the action than the remainder.

5.—*Sodium Dihydrogen Orthophosphate Monohydrate*,
 $\text{NaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$. $M = 138.0$.

W.	180°.	
	V.	N.
1606.5	120.4	0.98
1592.4	125.5	1.04
	Mean.....	1.01

Duplicate samples converted into metaphosphate by ignition each lost $2.06\text{H}_2\text{O}$ (calc. 2.00).

Action with carbide is in this case very slow in the cold, about 5 c.c. of gas being evolved per hour. At about 50° the rate increases quickly and then diminishes until the final value is reached, when the salt is dehydrated. In contrast, however, to the monohydrogen salt, it retains its constitutional water even at 180° .

6.—*Sodium Ammonium Hydrogen Orthophosphate Tetrahydrate*,
 $\text{Na}(\text{NH}_4)\text{HPO}_4 \cdot 4\text{H}_2\text{O}$. $M = 209.2$.

The gas evolved in this reaction, after measurement, was bubbled through a known volume of $N/10$ -hydrochloric acid, and the solution titrated with $N/10$ -alkali. In this way it was found that in each case a little ammonia was contained in the gas. The volume of this ammonia was calculated and was subtracted from the total volume to find the true value of V , the volume of acetylene. These figures are included in the following table:

170°.				
<i>W.</i>	<i>V</i> + NH_3 .	NH_3 .	<i>V.</i>	<i>N.</i>
482·1	110·1	10·2	99·9	4·12
482·5	111·0	11·0	100·0	4·12
			Mean.....	4·12

The action in the cold is very slow. It is seen from the table that the salt is rendered anhydrous at or below 170°. The part of the salt which loses ammonia must either lose constitutional water also, or else form the stable salt NaH_2PO_4 . Which of these happens cannot be determined from the above results, since the difference lies within the limit of experimental error, the loss of ammonia being only one-fifth of a molecule per molecule of salt after the mixture had been kept at 150° to 170° for an hour and a-half. The behaviour of salts containing ammonium will be discussed later.

7.—*Zinc Sulphate Heptahydrate*, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. $M = 287\cdot6$.

<i>W.</i>	Cold.		100°.	
	<i>V.</i>	<i>N.</i>	<i>V.</i>	<i>N.</i>
483·7	—	—	109·6	6·21
479·9	—	—	104·9	5·98
529·5	98·0	5·07	115·7	5·98
533·7	97·6	5·01	116·1	5·96
	Mean	5·04		6·03

The salt was recrystallised. Duplicate samples, dried in the oven to constant weight at 110°, each lost $5\cdot88\text{H}_2\text{O}$ (calc. $6\cdot00$). This observation may be compared with the statement by Müller-Erbach (*Math. Nat. Mitt. Berl. Akad.*, 1885, 201), that at 20° the salt reaches inappreciable vapour-tension after losing $5\frac{3}{4}\text{H}_2\text{O}$. At 170° the same samples lost $5\cdot93\text{H}_2\text{O}$.

With carbide in the cold, there was a short induction period followed by rapid action, the salt losing $5\text{H}_2\text{O}$, and then practically ceasing to act on the carbide. The dihydrate which is formed is well known. At 100° the salt is converted into the well-known and very stable monohydrate.

8.—*Magnesium Sulphate Heptahydrate*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$. $M = 246\cdot5$.

<i>W.</i>	110°.		140°.	
	<i>V.</i>	<i>N.</i>	<i>V.</i>	<i>N.</i>
544·4	135·6	5·85	—	—
537·0	132·6	5·80	—	—
469·2	—	—	121·6	6·08
467·3	—	—	119·6	6·01
	Mean	5·82		6·04

The salt was recrystallised and dried over partly dehydrated crystals of the same. After being heated to constant weight at 140° in the oven, duplicate samples lost 5.89 and 5.91 H_2O (calc. 6.00 ; compare last salt).

With carbide the action is similar to that of the zinc salt. In the cold, action almost stops when the salt has lost 4.9 to 5.0 H_2O ; but after this there is still very slow production of gas. This result indicates that a dihydrate is produced, as was the case with zinc sulphate; the compound $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ is evidently not so stable, however, as $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$. Graham observed that $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ in a vacuum at 22° loses about $5\text{H}_2\text{O}$, but no other evidence of the existence of a dihydrate has previously been produced.

When heated to 140° with carbide, the salt is converted into the monohydrate, as in the case of the zinc salt.

9.—*Cobalt Sulphate Heptahydrate*, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$. $M = 281.2$.

W.	140° .	
	V.	N.
561.5	125.4	5.98
563.2	124.9	5.94
	Mean	5.96

Selected crystals were used. When dried at 140° in the oven to constant weight, a sample of the salt lost $5.65\text{H}_2\text{O}$ (calc. 6.00).

The action with carbide was slower than in the last two cases, and did not give evidence of definite intermediate hydrates. At 140° the salt was, like the two preceding ones, converted into monohydrate.

10.—*Copper Sulphate Pentahydrate*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. $M = 249.6$.

W.	100° .	
	V.	N.
754.7	127.8	4.03
750.6	126.8	4.01
	Mean	4.02

Selected crystals were used.

The action of carbide in the cold is very slow and steady. At about 65° it proceeds quickly, and is soon completed at 100° , when the salt is converted into the monohydrate.

When further heating is tried, at about 140° a marked decrease in the volume of the gas occurs. This was followed up in a special experiment until five molecules of acetylene had been absorbed per atom of copper, the action being then still unfinished. No volatile products were observed; but the solid residue contained a

black substance insoluble in acid or ammonia, which, after extraction with water and acid, burnt easily, leaving a residue of copper oxide. It did not contain copper sulphide, and was evidently similar to the complex and somewhat indefinite copper compounds obtained by Söderbaum (*Ber.*, 1897, **30**, 760) by passing acetylene into aqueous solutions of certain cupric salts. Absorption of acetylene has not been observed with any salts here studied other than those of copper.

11.—*Potassium Copper Sulphate Hexahydrate*, $\text{K}_2\text{Cu}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$.

$M = 442.0$.

W.	65°.	
	V.	N.
800.3	110.0	5.79
801.6	108.9	5.72
	Mean	5.76

The salt was prepared by crystallising from a solution of cupric oxide in potassium hydrogen sulphate, washing with saturated solution of the salt itself, and drying with filter paper. The crystals so obtained were well formed and clear.

Action on carbide is extremely slow in the cold, but proceeds quickly at about 60°, and ceases after some hours at 65°, when 5.76H₂O out of 6H₂O have reacted. An experiment in which higher temperatures were used gave 5.6H₂O at 100°, suggesting that the absorption mentioned in the last case had already begun. This was confirmed, as the volume of gas began to diminish very perceptibly at 110°.

12.—*Ammonium Ferrous Sulphate Hexahydrate*,

$(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$. $M = 392.2$.

W.	100°.	
	V.	N.
656.7	104.0	5.92
663.3	103.2	5.81
	Mean	5.86

The action was exceedingly slow in the cold, but complete at 100° after one to two hours, when the salt was nearly anhydrous, although, as in the case of the last salt, not completely so.

It would be expected that ammonia would be produced on heating, especially as calcium hydroxide is present in considerable quantity as a product of the action; but the gas on being tested was found to be free from any trace of alkalinity.

13.—*Ammonium Oxalate Monohydrate*, $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

M = 142.1.

W.	100°.	
	V.	N.
1484.5	106.6	0.97
1480.9	103.7	0.95
	Mean	0.96

The salt was a good commercial sample and was not recrystallised.

With carbide, action was very slow in the cold, but became quicker on warming, and after reaching 70° was almost complete, as Dupré observed (*loc. cit.*). Heating to 100° yielded a final result when the salt was rendered anhydrous without loss of any ammonia, as a test showed. When the mixture was heated to 160° for an hour and a-half, the gas was found to contain a small trace of ammonia.

Of the five ammonium salts examined, three (double sulphates) gave off no ammonia when heated with carbide; ammonium oxalate gave off none at 100° and only a trace at 160°; and microcosmic salt at some temperature below 170° gave off a small amount. It is possible that the readily hydrolysed microcosmic salt gave off a little ammonia before the drying process was complete, whilst the other ammonium compounds did not, nor were they acted on when dry on being heated with the calcium hydroxide produced during the drying process. The trace of ammonia obtained with ammonium oxalate was evidently the result of decomposition of the dry salt itself.

Alums. 14.—*Ammonium Iron Alum*, $(\text{NH}_4)\text{Fe}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

M = 482.3.

W.	Cold.		145°.	
	V.	N.	V.	N.
479.4	94.7	9.08	113.8	10.90
479.2	93.9	9.00	113.7	10.89
	Mean	9.04		10.90

Selected amethyst-coloured crystals were used.

When heated at 100° in the oven to constant weight, the salt melted, and duplicate samples lost 42.68 and 42.77 per cent. of their weight, with formation of a little insoluble matter, presumably basic salt (calc. for $12\text{H}_2\text{O}$, 44.83, and for $11\text{H}_2\text{O}$, 41.09 per cent.).

With carbide, action in the cold proceeded with a velocity little short of that attained by sodium carbonate or sulphate, and the salt lost $9\text{H}_2\text{O}$, being thus converted into a trihydrated double salt

(or possibly a mixture of ammonium sulphate with a hexahydrated ferric sulphate). On heating to 145° , the further action is quickly complete, and shows conversion into a monohydrate.

The gas was tested in the same way as that from microcosmic salt and found to contain no ammonia.

There is no previous record of the hydrates of ferric ammonium sulphate (or of ferric sulphate) which have been observed here.

15.—*Ammonium Aluminium Alum*, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.
 $M = 453\cdot5$.

W.	50°.		160°.	
	V.	N.	V.	N.
478·5	100·3	9·05	117·3	10·59
479·4	100·0	9·01	115·3	10·39
	Mean.....	9·03		10·49

The salt, dried at 160° in the oven, was found to have lost ammonia and the greater part of its water.

Action with carbide was extremely slow in the cold, but at 50° it suddenly increased rapidly and then stopped, when the salt was found to have lost $9\text{H}_2\text{O}$, as did the last alum. Heated at 160° , the result was constant when the salt had lost $10\cdot5\text{H}_2\text{O}$, indicating either a double salt with $1\cdot5\text{H}_2\text{O}$ or else a trihydrate of aluminium sulphate.

The gas was proved in this case, also, to be free from any ammonia.

Müller-Erzbach (*Ber.*, 1889, **22**, 3181) notes that 9 molecules of water are less firmly attached than the other three, among which last, however, he apparently found no further differences, such as are shown by the above results.

16.—*Potassium Aluminium Alum*, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$. $M = 474\cdot3$.

W.	170°.	
	V.	N.
453·7	103·6	10·31
446·2	101·8	10·31
452·9	102·3	10·20
449·5	102·2	10·27
	Mean	10·27

Selected crystals were used, which analysis showed to be pure. When dried at 110° in the oven for two hours, a sample of the salt lost $9\cdot70\text{H}_2\text{O}$ (calc. $12\cdot00$); at 110° for four and a-half hours more it had lost $9\cdot90\text{H}_2\text{O}$; and at 130° for twenty-three hours more the loss amounted to $10\cdot42\text{H}_2\text{O}$.

Action with carbide is very slow in the cold, but at about 50° it becomes rapid. Experiments in which the amount of action at this temperature was measured showed that about $9\text{H}_2\text{O}$ were acted on; but there is no point of complete stoppage, such as occurred with the last alum. Kraut (*Ber.*, 1875, **8**, 1630; 1877, **10**, 456) found that the salt lost $9\text{H}_2\text{O}$ over sulphuric acid, and Müller-Erbach (*loc. cit.*) also found evidence of the existence of the trihydrate. Action at 100° went on to the same extent as at 170° , the result being very similar to that with the last salt, which lost $10\cdot5\text{H}_2\text{O}$. It is noteworthy that drying in the oven resulted eventually in practically the same loss as occurred with carbide.

17.—*Potassium Chromium Alum*, $\text{KCr}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$. $M=499\cdot6$.

W.	100°.	
	V.	N.
528·9	106·4	9·57
530·1	106·0	9·52
572·0	115·5	9·61
	Mean... ..	9·57

Duplicate samples dried at 175° in the oven to constant weight gave losses corresponding with $11\cdot12\text{H}_2\text{O}$ and $11\cdot15\text{H}_2\text{O}$ (calc. $12\cdot00$); but much insoluble matter was formed.

With carbide, action was slow in the cold, but became rapid at about 35° , when between 5 and 6 molecules of water were acted on. In this case Müller-Erbach found that 6 molecules of water were more easily removed than the remainder of the water. At 100° , as shown above, 9·6 molecules of water were acted on, which quantity was not increased by heating at 170° . It is probable that we are here dealing with one or more of the complex sulphates the formation of which characterises chromium compounds as distinct from those of aluminium and iron.

Remark on the Alums.

Statements by different observers concerning the behaviour of the alums when heated or otherwise dehydrated vary. For instance, Dammer quotes Kraut (*loc. cit.*) to the effect that $\text{KAl}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ loses 9 molecules of water in a vacuum over sulphuric acid, whilst Jüttke (*Inaug. Diss. Berlin*, 1887) states that in these circumstances it loses 9·5 molecules of water. Again, Müller-Erbach states that $\text{KCr}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$, after losing 6 molecules of water over sulphuric acid, loses $4\cdot5\text{H}_2\text{O}$ more on prolonged heating at 116° ; Jüttke maintains that it is completely dehydrated by heating at 100° without formation of any insoluble matter; whilst

my own results, obtained by heating in the oven at 175° , show that it is stable after sustaining a loss corresponding with $11\cdot1\text{H}_2\text{O}$, but at the same time forms a considerable amount of matter insoluble in water and only very slowly soluble in boiling dilute hydrochloric acid. Several other instances might be cited. It is thus evident that the result obtained varies according to the procedure adopted, and there is some need of a fuller investigation of the facts.

18.—*Sodium Biborate Decahydrate*, $\text{Na}_2\text{B}_4\text{O}_7\cdot 10\text{H}_2\text{O}$. $M=382\cdot 2$.

W.	170°.	
	V.	N.
397·2	95·7	8·77
398·0	95·9	8·77
445·0	106·9	8·75
451·0	109·1	8·81
	Mean	8·77

Duplicate samples, when fused, each lost $10\cdot01\text{H}_2\text{O}$ (calc. $10\cdot00$). Duplicate samples, dried at 170° to constant weight, lost $8\cdot61\text{H}_2\text{O}$ and $8\cdot62\text{H}_2\text{O}$.

Action with carbide is slow in the cold, but is final after heating to 170° , when 8·8 molecules of water have been acted on. It will be seen that almost the same result was achieved by continued drying in the oven at the same temperature. This is not the only case which has been mentioned in which careful experiments with carbide and in the oven yield results showing no integral molecular dehydration. In some cases this may be due to the composition of the salt differing from that shown by the formula. In others there are strong reasons for taking the salt as pure. In the present case this is proved by the fusion tests. A satisfactory explanation of this fact is wanting, as it appears to be contrary to the theory of the vapour pressure of hydrates.

19.—*Sodium Thiosulphate Pentahydrate*, $\text{Na}_2\text{S}_2\text{O}_3\cdot 5\text{H}_2\text{O}$.
 $M=248\cdot 2$.

W.	100°.	
	V.	N.
602·3	124·3	4·88
587·4	120·2	4·84
	Mean	4·86

Action in the cold proceeded quickly until about 4·3 molecules of water had reacted, after which it continued at a considerably slower rate. At 100° action was over at a value of $4\cdot9\text{H}_2\text{O}$. In this case

the deficiency may be accounted for by the fact that the heat of the first action had fused some of the salt into lumps, an occurrence not observed with any other salt.

20.—*Oxalic Acid Dihydrate*, $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. $M = 126.0$.

W.	Cold.		100°.	
	V.	N.	V.	N.
730.8	116.7	1.92	—	—
729.2	118.6	1.95	—	—
633.5	99.3	1.88	101.4	1.92
633.2	95.7	1.81	98.7	1.87
	Mean.....	1.89		1.90

Titration of the crystals with permanganate gave $1.92\text{H}_2\text{O}$ (calc. 2.00).

The carbide action is here quick and steady, causing complete dehydration without external application of heat being necessary.

It is noteworthy that oxalic acid as such has no action on either the carbide or the calcium hydroxide which is a product of the dehydration action. Heating the mixture to 170° was found to cause decomposition of the oxalic acid with evolution of carbon dioxide which was found in the gas. The explanation of both of these observations is probably to be found in the special dryness of the materials.

21.—*Barium Chloride Dihydrate*, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. $M = 244.3$.

W.	170°.	
	V.	N.
1307.5	106.1	1.89
1310.4	107.1	1.90
	Mean	1.90

Ignition of duplicate samples gave a loss in each case of $2.00\text{H}_2\text{O}$ (calc. 2.00).

With carbide, action was very slow in the cold, but went on more quickly at higher temperatures. At 170° it had stopped, the salt being rendered practically anhydrous.

22.—*Chloral Hydrate*, $\text{CCl}_3 \cdot \text{CHO} \cdot \text{H}_2\text{O}$. $M = 165.4$.

W.	100°.	
	V.	N.
1478.3	91.2	0.97
1474.2	89.8	0.96
	Mean	0.96

Clear dry crystals were used.

With carbide this compound behaved in a manner similar to that of many hydrated salts. In the cold, action proceeded steadily and slowly; rather faster on heating at 100° , when the compound lost practically all its water.

Summary.

1. When certain hydrated salts, such as sodium carbonate and sulphate decahydrates and a few others, are powdered and intimately mixed with excess of powdered calcium carbide, acetylene is generated at once with evolution of heat, and the action is complete in less than a minute. Other salts require more or less heating to bring about rapid action.

2. The rapidity of the production of gas is to be explained, not by action of the carbide on the solid hydrate itself, but by its action on water vapour which the hydrate emits, the possibility of any check to the rate of dehydration by return of water molecules to the hydrate surface being precluded by intimate contact of the two materials.

3. After standardisation of the method with pure water, the volume of gas evolved can be used as a measure of the quantity of water of crystallisation which has been acted on by the carbide.

4. With some of the twenty-two hydrated salts examined, action either in the cold or at higher temperatures ceases only when the salt has become anhydrous; in other cases, relatively stable lower hydrates are formed. Some of the lower hydrates met with in this way have not previously been shown to exist.

5. Of the five ammonium salts examined, three did not lose any trace of ammonia, even although heated at temperatures from 100° to 160° in the presence of calcium hydroxide produced during dehydration. In a fourth case a mere trace of ammonia was observed.

6. Crystalline acids and acid salts, so far as they have been studied, do not react as acids with either the calcium carbide or the calcium hydroxide product with which they are mixed.

In conclusion, I wish to record my obligation to Professor Orme Masson for guidance throughout the course of the work.

THE UNIVERSITY OF MELBOURNE.

LXII.—*The Examination of the Atmosphere at Various Altitudes for Oxides of Nitrogen and Ozone.*

By WALTER HAYHURST and JOHN NORMAN PRING.

ALTHOUGH much work has been done on the question of the presence of ozone in the atmosphere, and many attempts have been made to estimate this gas quantitatively, yet on account of the methods used the results are nearly all inconclusive, and the available evidence on the problem is most contradictory.

One of the oldest tests, which was established by Schönbein, consisted in exposing to the atmosphere a paper which had been dipped in a solution of potassium iodide and starch, when a blue colour, due to the liberation of iodine, was supposed to indicate the presence of ozone. This test, however, is quite untrustworthy, for oxides of nitrogen, which are natural constituents of the atmosphere, hydrogen peroxide, and chlorine also give a similar reaction.

Cloëz (*Compt. rend.*, 1856, **43**, 38; 1861, **52**, 527) showed that these papers are also coloured by acid vapours, nitrous fumes, and by the vapours of essential oils which are given off from certain trees, and by the action of sunlight in presence of moisture.

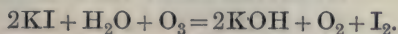
Moffatt (*Brit. Ass. Report*, 1870, 61) published a note on the results of atmospheric ozone tests conducted daily for twenty years, using the potassium iodide and starch papers. No information, however, is given of his method of conducting the tests, so that his conclusions as to the presence of ozone in the atmosphere, and its variation from time to time are valueless. Houzeau (*Ann. Chim. Phys.*, 1872, [iv], **27**, 5; *Compt. rend.*, 1872, **74**, 712) again drew attention to the unsatisfactory nature of potassium iodide and starch papers as a test for ozone, and suggested the use of a paper impregnated with potassium iodide and litmus, when the alkali formed by the ozone turns the paper blue. In this way a distinction can be made between this gas and oxides of nitrogen and chlorine, which do not, of course, liberate free alkali. This method, however, is rendered very uncertain by the fact that the free iodine combines with the paper, giving a brown colour, which masks the blue colour produced by the alkali. Even in solution a coloration is produced by some action between the iodine and the litmus. Similarly, if phenolphthalein or rosolic acid be employed as indicator, the marking effect of the iodine is too serious to permit the test to be employed with any certainty.

Engler and Wild (*Ber.*, 1896, **29**, 1940) made an extensive investigation on the detection of ozone, and conclude as a result

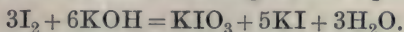
that this gas is present in the atmosphere. Large quantities of air were passed first over finely-divided chromic acid to remove hydrogen peroxide, and then led into a glass tube containing a paper impregnated with manganese chloride, which is turned brown by ozone. This brown coloration is stated to be easily distinguishable from that which, as pointed out by Schöne, is produced by ammonia and ammonium carbonate.

Wurster (*Ber.*, 1888, **21**, 921) and Arnold and Mentzel (*Ber.*, 1902, **35**, 1324) recommend the use of tetramethyldiaminodiphenylmethane as a qualitative test for ozone. In the experiments made by the present authors, this test was not found to be at all a delicate one, and, in any case, the blue and yellow colours due to oxides of nitrogen appear to mask the effect of ozone, and the colours produced are not permanent.

Hatcher and Army (*Amer. J. Pharm.*, 1900, **72**, 9) made use of two methods for the quantitative estimation of atmospheric ozone, namely: (1) Large quantities of air were passed through a potassium iodide solution, when ozone reacts as follows:



The potassium hydroxide and iodine then slowly react to form potassium iodate and iodide according to the equation:



The iodate is detected by means of the free iodine, which is again liberated on acidifying, and which can be estimated quantitatively by titrating with sodium thiosulphate.

(2) The second method consisted in passing air through a solution of potassium arsenite. Ozone oxidises this to arsenate, and its amount can be calculated by the estimation of the loss of arsenite. The two methods gave very different results, and a complete distinction does not seem to have been made between ozone and other constituents of the atmosphere which could affect the reagent.

Variation of Amount of Ozone in Atmosphere with Altitude.

Thierry (*Compt. rend.*, 1897, **124**, 460) estimated the amount of ozone in the atmosphere, at various altitudes, on Mont Blanc, and concludes that the amount of this gas increases with the height.

Henriet and Bonyssy (*Compt. rend.*, 1908, **146**, 977) made daily observations of the amount of ozone and of carbon dioxide in the atmosphere at ground level, and concluded that there is a relation between the amounts of these gases, a maximum of ozone occurring with a maximum of carbon dioxide. They consider that ozone is formed by ultra-violet light in the higher atmosphere. In this work

no means were apparently adopted to distinguish between ozone and other active gases. The results expressed below, in tabular form, of the main workers on the question of atmospheric ozone show how conflicting is the evidence on the subject:

Author.	Amount of ozone in milligrams per cubic metre air (1000 litres).	
	Maximum.	Minimum.
Houzeau (<i>loc. cit.</i>)	2·8	—
Schöne (<i>Brochure</i> , Moscow, 1897).....	100·0	10 0
H. de Varigny (<i>Smithsonian and Miscell. Coll.</i> , 39, 27)	0·03	0·01
Hatcher and Arny (<i>loc. cit.</i>)—		
Potassium iodide method	158·0	31·6
Potassium arsenite „	34·0	8·0
Thierry (<i>loc. cit.</i>)—		
At 1000 metres altitude	0·039	—
At 3000 „ „	0·094	—

In the use which has hitherto been made of potassium iodide for the detection of ozone, no special precautions seem to have been taken to exclude the effect of sunlight, which causes a complication in this reaction by decomposing the potassium iodide.

The present investigation deals with the detection and quantitative estimation of atmospheric ozone at ground level at several places in this country, and at various altitudes, ranging up to twelve miles. The main part of the work at ground level and intermediate altitudes was carried out on Glossop Moor, in Derbyshire, at the Kite Station of the Meteorological Department of this University.

The method used consisted in allowing the air at a known velocity to blow through a vessel, by means of which it was projected on to the surface of a solution of pure potassium iodide, which was protected from the action of light. The solution was then carefully examined for free iodine, free alkali, and potassium iodate. In this way, an estimation could be made of the ozone (together with hydrogen peroxide) and of the oxides of nitrogen.

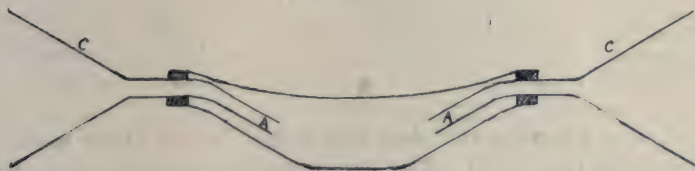
The degree of accuracy to which this reagent can be relied on for detecting ozone was ascertained by dissolving a weighed quantity of iodine in potassium iodide solution, and finding the greatest dilution at which the yellow colour of the solution was still perceptible. Working with 2 c.c. of the solution, the presence of 0·01 milligram of iodine, which corresponds with 0·0019 milligram of ozone, can be detected with certainty in absence of starch paste, and an accurate titration of this amount could be made with *N*/1000-sodium thiosulphate solution. It was also found that potassium iodate in presence of excess of iodide could be accurately estimated at a correspondingly high dilution. The actual reaction between ozone in very small quantities and pure potassium iodide

was examined by passing the gas from a Siemens ozoniser through a concentrated solution of this reagent until 0.1 milligram of iodine per c.c. was liberated. By titrating within a few minutes, it was found, after first removing the free iodine by sodium thiosulphate, that the potassium hydroxide formed was approximately equivalent in quantity to the iodine which was liberated on decomposing the potassium iodate. After keeping for a week, no diminution in the amount of alkali or increase of iodate could be detected.

Description of Apparatus.

The apparatus which was finally used in the atmospheric work consisted of a glass boat-shaped bulb, provided with inlet and outlet tubes opposite to each other (Fig. 1). The outside ends of the tube were widened into conical funnels, *C, C*, and the inside ends *A, A*, projected some way inside the bulb to act as a trap and prevent loss of the reagent during any tilting of the vessel. The vessels used were of such a size as to contain about 34 c.c. of the

FIG. 1.



reagent when held in any position. The diameter of the ends of the funnels was about 10 cm., and the internal diameter of the tube from 9 to 10 mm. During exposure to the atmosphere this apparatus was always kept parallel to the direction of the wind by a mechanical arrangement, and could be conveniently attached to a kite wire when the kite was being flown in a moderate and steady wind in such a way as to keep level and point towards the wind.

The bulb was tested for its efficiency in absorbing ozone by preparing small quantities of this gas with a Siemens ozoniser and passing it, together with an excess of air, over the reagent in the vessel, and then through a second vessel. When the flow of air amounted to about 6 litres per minute, all the ozone was taken up in the first vessel, and no appreciable liberation of iodine occurred in the second, thus demonstrating the efficiency of the absorption.

The experiments described below on the detection of ozone at Glossop Moor, at ground level, and at intermediate altitudes (up to 8500 feet) were of a purely qualitative nature, as in no case was any trace of ozone detected.

Attempts were in addition made to compare the amount of oxides of nitrogen at different altitudes.

Series I (a). Experiments at Ground Level.—Some fifteen experiments were conducted at ground level (1100 feet above sea level) between the dates April 19th and July 22nd, 1909. The vessel described above was exposed for periods of from two to six hours. Care was taken in each case to protect the reagent from the action of sunlight. The amount of iodine liberated in the total solution varied, in the different experiments, from 0.15 to 0.75 milligram, but in no case was there any trace of alkali or of iodate.

(b) Experiments at Intermediate Heights.—Some fifteen successful experiments on the detection of ozone were carried out at intermediate heights by means of kites. The results of a few of these are tabulated below:

Date.	Amount of iodine liberated in milligrams.	Alkali.	Potassium iodate.	Maximum height of kite above ground.
May 18th, 1909.....	1.37	nil	—	8500 feet
„ 20th, „	0.89	„	—	3200 „
„ 20th, „	0.55	„	—	2600 „
„ 21st, „	0.925	„	—	4200 „
June 3rd, „	0.783	„	—	4500 „
July 21st, „	—	„	nil	about 5000 „
„ 22nd, „	—	„	„	„ 5000 „

A similar quantity of iodine was found in the other cases, and no iodate or free alkali. The exposures in the above experiments were made for from two to four hours, and the wind velocity varied from 20 to 45 miles per hour.

Estimation of Comparative Amounts of Oxides of Nitrogen at Various Altitudes.—These comparative measurements were attempted by taking two similar absorbing vessels, and exposing one to the atmosphere at ground level, while the other was attached to the kite during the same interval and exposed at known altitudes. A knowledge of the altitude of the kite and the wind velocity was obtained by means of the Dines recording meteorograph (compare *Nature*, 1910, **83**, 220), which was attached to each kite, whilst that at ground level was indicated by an anemometer. The amount of air which was passed through the vessels was assumed to be proportional to the wind velocity, and at high altitudes the volume was corrected for the diminished pressure. To correct for inequalities in the size of the two vessels an atmospheric test was carried out in which they were used side by side, when it was found that 13 per cent. more iodine was liberated in one than in the other. This correction was consequently added to the others.

The reagent employed in these measurements consisted of pure

potassium iodide * dissolved in distilled water, in the ratio of 50 grams of salt to 100 grams of water.

Thirty experiments on these comparative estimations were attempted, the six most successful being tabulated below:

Date.	Time.	Direction of wind.	Minimum temp.	Maximum height in feet.	Ratio of oxides of nitrogen
					in upper to that in lower atmosphere.
May 18th, 1909	(noon) S.	-12°	8500	2.23 : 1
„ 20th,	„ S.	+7	3200	1.74 : 1
„ „	(evening) S.	-5	2600	1.76 : 1
„ 21st,	(morning) S.E.	+6	4200	1.20 : 1
June 3rd,	(noon) S.E.	-1	4500	0.93 : 1
„ „	(evening) E.	-1	4500	0.90 : 1

The ratio gives approximately the proportion of oxides of nitrogen at higher altitudes to that at ground level for equal volumes of air. An error, which would make this ratio too low, is due to the fact that with the higher wind velocities in the upper atmosphere a larger percentage of the gas would escape condensation in the reagent in the vessel.

These results seem to indicate, consequently, a rather greater quantity of oxides of nitrogen at higher altitudes than at ground level, although the method used can only serve as a rough approximation. The total amount of these oxides present was found to vary from day to day, and there appeared to be much less present after rain.

Examination for Free Chlorine.—In order to ascertain if any free chlorine was present in the atmosphere, two tests were made with the above apparatus, but containing pure sodium hydroxide solution (prepared from sodium and distilled water). These experiments were conducted at ground level, one being exposed for four hours in a moderate wind, and the other for seven hours and a-half in a wind of four miles per hour. No trace of chlorine could be detected in the reagent afterwards by neutralising and adding silver nitrate.

Colorimetric Tests with Tetramethyldiaminodiphenylmethane.

A small quantity of the tetramethyl base was dissolved in methyl alcohol, and then poured on to a piece of white cotton wool, a portion of which was attached to the kite wire, while the remainder was exposed at ground level.

A green colour was often obtained, sometimes yellow, and sometimes a bluish tint, but the violet of ozone was never obtained. The other colours were doubtlessly caused by oxides of nitrogen.

* Merck's pure neutral.

As mentioned above, however, this test was not found to be a satisfactory one for ozone.

Series II. Examination of Air at Ground Level in Various Localities.—A series of tests was conducted on the air over the sea and in mountain districts away from any possible contamination through organic matter. The absorbing vessels used were of the spherical type described below, and contained about 10 c.c. of the reagent.

No. 1.—Conducted in the Isle of Man in September, 1909, at an elevation of 300 feet above the sea and 6 feet above the ground. Vessel exposed for two hours, at noon, to a north wind of about 17 miles per hour. The reagent used consisted of 100 parts of potassium iodide to 100 parts of water by weight, and afterwards contained 0.16 milligram of free iodine and no iodate or alkali.

No. 2.—Apparatus exposed on sailing vessel in Irish Sea in the afternoon to about 30 miles of wind, direction of wind north. The reagent afterwards contained 0.08 milligram of iodine and no iodate or alkali.

No. 3.—Vessel exposed in Cardiganshire, near the coast, for twenty-eight hours, in January, on the summit of a hill 600 feet high. Direction of wind WSW, and direct from the sea. Velocity 20 to 40 miles per hour. Iodine liberated 1.3 milligram, iodate nil, alkali nil.

No. 4.—Vessel exposed at Aberystwyth Observatory for twenty hours. Wind S.W. direct from sea; velocity 20 to 40 miles per hour. Iodine liberated 1.2 milligrams, iodate nil, alkali nil.

No. 5.—Vessel exposed at noon at Wenlock (West Salop), on August 23rd, 1909, to about 20 miles of wind. No iodate found. Direction of wind W.

No. 6.—Vessel exposed in afternoon to 30 miles of west wind at Wenlock. No iodate found.

Series III. Examination of the Atmosphere at High Altitudes.—In these experiments use was made of the free balloons which are periodically sent up by the Meteorological Department of this University. These balloons ascend with a velocity of about ten miles per hour, and attain a height of about twelve miles, when they burst, and the skin acts to a certain extent as a parachute, checking the velocity of the instruments as they come to the ground. The absorbing vessel employed was of smaller dimensions than that used in the kite work, and the bulb was made spherical (Fig. 2).

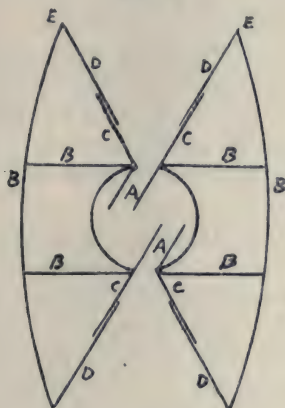
The internal diameter of the inlet and outlet tubes, *A, A*, was 1 cm., and the diameter of the bulb 5 cm. The apparatus was encased in a cage made of steel spring wire, and the glass funnels,

C, C , were extended by attaching paper cones, D, D , the diameters of which, at the wide ends, were 7.5 cm.

This form of vessel seemed specially suited for bringing a large quantity of air in contact with the reagent, with the minimum of resistance to its passage. By placing some fuming liquid inside and allowing the air to blow through, this was shown to assume a rapid circulatory motion inside the bulb. The glass bulb was enamelled black on the outside, and, in addition, covered with a layer of black cloth, to exclude the light. This apparatus was suspended vertically from the balloon by means of string attached at E, E , and the upward and downward motion of the balloon through the air caused the necessary circulation of air through the bulb.

The ascent was always made at night to avoid further the com-

FIG. 2.



plicating effect of bright sunlight; 5 to 7 c.c. of a solution of pure potassium iodide, containing 100 grams of salt to 100 grams of water, were used as the reagent, and the whole apparatus, together with an attached note to the finder, weighed about 2 oz. The temperature and height attained during each ascent were recorded on an attached thermo- and baro-graph.

Reaction at Low Temperatures.

The minimum temperature encountered by these balloons is about -55° , and as the cryoscopic point of the potassium iodide solution is -22° , it was thought necessary to ascertain if any reaction takes place between ozone and the reagent, when in the solid condition, below this temperature. For this purpose a current

of ozonised air was passed on to the surface of the reagent in two test-tubes placed in series, the first being cooled by means of ether and solid carbon dioxide, and the second being kept at the ordinary temperature.

The temperature of the first was read by means of a pentane thermometer. The inlet tube in each test-tube terminated about 4 cm. above the level of the reagent. The ozone which escaped absorption in the cold tube would, in this way, be led over the reagent in the second. It was found that when the temperature of the first reagent was kept at -56° , more ozone was always absorbed here than in the second, which shows, in a rough manner, that the reaction readily takes place at these low temperatures with the solid reagent.

Moreover, in the actual flights, the solution would probably not entirely freeze for some time after the surrounding temperature had fallen below the cryoscopic point, on account of the high latent and specific heat of the solution.

The volume of air which passed through the vessel during an ascent of 10 miles and descent was estimated to be between 0.1 and 0.3 cubic metres. From this, it was calculated that the volume of air dealt with in the experiments at ground level described above (Series I and II) was, in each case, from 1 to 10 cubic metres.

Experiments.—(1) Ascent made on August 3rd, 1909, at nine o'clock p.m. Apparatus recovered near Selby, in Yorkshire, about 50 miles away. Maximum height recorded on barograph about 10 miles. Eleven c.c. of reagent placed in vessel, and about 7 c.c. returned. On titrating with $N/500$ -sodium thiosulphate, there was found to be 0.12 milligram of free iodine in solution, and, on acidifying, a further 0.13 milligram of iodine was liberated. This corresponds with 0.048 milligram of ozone, allowing one-half of this gas to have formed iodate.

(2) Ascent made on February 2nd, 1910, at 5.30 p.m. Apparatus recovered from Knaresborough, Yorkshire, on February 21st. Maximum height attained, $7\frac{1}{4}$ miles. Amount of free iodine, less than 0.06 milligram. After acidifying, less than 0.03 milligram was liberated, which corresponds with less than 0.01 milligram of ozone. No free alkali present.

(3) Ascent made on March 18th, 1910, at night. Vessel contained 8 c.c. of reagent, and was returned from South Wales on March 31st with 6 c.c. of reagent remaining; maximum height attained, $8\frac{1}{2}$ miles. Free iodine (calculated for 8 c.c.), 0.21 milligram. Iodine liberated after acidifying, 0.13 milligram, corresponding with 0.048 milligram of ozone.

The amount of oxides of nitrogen at these high altitudes appears from these results to be less than that of ozone.

Conclusions.

In the above work, means were devised to carry out accurately a qualitative examination of the atmosphere for the presence of ozone and oxides of nitrogen at various altitudes.

Experiments were made systematically above Glossop Moor, in Derbyshire, during three or four months in summer, and were supplemented by a number of tests on sea and mountain air at various places in this country. It was found that oxides of nitrogen were always present in quantities which vary largely from time to time, and that the amount of ozone was, in every case, too small to be detected in the experiments conducted at ground level and at intermediate altitudes (that is, up to 8000 feet). It was shown, in consequence, that the amount of ozone is less than 0.003 milligram in the quantity of air dealt with in each experiment (that is, between 1 and 10 cubic metres), or, expressed by volume, less than 1 part in 4,000,000,000 parts of air.

Experiments at very high altitudes (ranging up to 10 miles) were carried out with the help of free balloons, and in these the presence of small quantities of ozone, averaging about 0.04 milligram in 0.1 to 0.3 cubic metre of air, was detected (or about one part in three to nine million parts of air, by volume), and the quantity of oxides of nitrogen was shown to be less than this.

Further measurements on the amounts of these gases at high altitudes are now in progress.

In conclusion, we wish to express our indebtedness to those in charge of the Meteorological Department for their kind assistance in this work.

ELECTROCHEMICAL LABORATORY,
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LXIII.—*Amphoteric Metallic Hydroxides. Part II.*

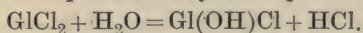
By JOHN KERFOOT WOOD.

IN a previous paper (Trans., 1908, **93**, 411) the author described experiments made with arsenious and aluminium hydroxides, with the object of comparing their basic and acidic affinities. As was there pointed out, the above two substances are amphoteric hydroxides of different types; arsenious hydroxide is appreciably soluble in water, and is more highly acidic than basic; aluminium hydroxide, on the other hand, is practically insoluble in water, and is more basic than acidic. There are a number of other metallic hydroxides of the latter type, and the results obtained in the investigation of the amphoteric characters of several of these substances form the subject matter of the present communication.

The hydroxides which have been examined are those of glucinum, zinc, and lead. All these are obviously of an amphoteric nature, since they are soluble, not only in acids, but also in solutions of alkaline hydroxides.

Ley (*Zeitsch. physikal. Chem.*, 1899, **30**, 199; *Ber.*, 1897, **30**, 2194) and Bruner (*Zeitsch. physikal. Chem.*, 1900, **32**, 132) have already conducted experiments to determine the amount of hydrolysis in solutions of salts of the above metals, the method used being that based on the inversion of sucrose. In the present series of experiments various methods were employed to arrive at the hydrolysis of solutions of the chlorides of the metals in question, a method which was suitable in one case proving to be inapplicable in others. The methods used will therefore be referred to under the headings of the individual metals.

In all three cases the amount of hydrolysis in a solution of the chloride is small. It is possible, therefore, to apply the same reasoning as was applied to the case of aluminium chloride (Wood, *loc. cit.*), and to say that the course of the hydrolysis of, say, glucinum chloride is represented by the equation:



Taking the total chlorine concentration as unity, and the concentration of the hydrochloric acid as x , the concentrations of the basic glucinum chloride and the normal chloride will be represented by x and $1 - 2x$ respectively, so that the conditions for equilibrium in a solution of glucinum, zinc, or lead chloride will be represented by the equation:

$$\frac{x^2}{(1 - 2x)v} = h \text{ (a constant).}$$

As x can be found experimentally, and v , the volume which contains one gram-molecule of the salt, is known, the value of the constant can be calculated, and hence the amount of hydrolysis in solutions of any concentration can be ascertained.

The hydrolysis takes place, of course, by virtue of the weaker hydroxyl ion of the hydroxides. Knowing the value of the hydrolysis constant, we can find the affinity of the weaker hydroxyl by means of the equation:

$$\frac{k_b}{K} = \frac{1}{h},$$

$$\text{or } K_b = \frac{1}{h} \times 1.21 \times 10^{-14}.$$

The other hydroxyl group is probably much stronger than the one the strength of which is arrived at in the above way.

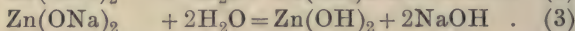
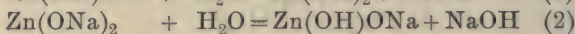
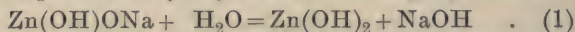
With regard to the acidic character of the hydroxides, Hantzsch (*Zeitsch. anorg. Chem.*, 1902, **30**, 302) has determined the electrical conductivity of solutions of sodium hydroxide, to which varying amounts of the other hydroxides have been added. From his results he concluded that of the three hydroxides in question that of lead is the strongest, and that of zinc the weakest acid. He also concluded that the hydroxides behave as monobasic acids, no evidence being found by him for the existence of ions such as ZnO_2^- .

In addition to the work of Hantzsch, Rubenbauer (*Zeitsch. anorg. Chem.*, 1902, **30**, 331) has determined the solubility of the hydroxides in various solutions of sodium hydroxide, and Haber and van Oordt (*Zeitsch. anorg. Chem.*, 1904, **38**, 377) have made similar determinations in the case of glucinum. The former pointed out that the influence exerted by the concentration of the alkali solution on the solubility of the other hydroxides is much greater in the case of zinc than with lead and glucinum, the influence being least in the case of the latter.

The experiments of the author were of the nature of solubility experiments. The hydroxide under examination was mixed with solutions of sodium hydroxide of varying concentration in bottles made of "resistance glass," and left in the thermostat at 25° until the solution attained a constant composition, the latter point being determined, of course, by repeated analyses. The accuracy of the results was tested as follows. The solubility of zinc or other hydroxide must necessarily be practically zero if the concentration of the sodium hydroxide is zero, for the hydroxides are practically insoluble in water. It follows, therefore, that the curve drawn through the points obtained by plotting sodium concentrations as abscissæ and zinc, glucinum, or lead as ordinates must, if the

experimental results are correct, pass, on extrapolation, through the origin. This condition was fulfilled in every case.

Knowing the solubility of the hydroxide in the solution of sodium hydroxide, the amount of hydrolysis in a solution of sodium zincate or other salt can be calculated by the method previously described for sodium metaluminate (Wood, *loc. cit.*). The question is complicated, however, in the present case by the fact that the equation representing the hydrolysis is not definitely known. Taking sodium zincate as an example, the hydrolysis of solutions of that compound might be represented by any of the following equations:



In any such solution the hydrolysis constant is calculated from the equation:

$$\frac{[\text{Acid}] \times [\text{Base}]}{[\text{Salt}]} = \text{constant.}$$

If for each of the above actions the total concentration of zinc and sodium be represented respectively by a and b , and if x represent the amount of $\text{Zn}(\text{OH})_2$ in (1) and (3) and of $\text{Zn}(\text{OH})\text{ONa}$ in (2), then, according to whether equation (1), (2), or (3) represents the hydrolysis of sodium zincate, the hydrolysis constant will be equal to

$$\frac{x(b-a+x)}{a-x}, \quad \frac{x(b-2a+x)}{a-x} \quad \text{or} \quad \frac{x\left(\frac{b}{2}-a+x\right)^2}{a-x}$$

respectively.

The value of x is experimentally indeterminate, but it must be constant no matter what the concentration of the alkali, for it is really the solubility of zinc hydroxide in water. The hydrolysis constant is also independent of the concentration. By equating the results obtained by the analysis of two solutions of different concentration, the following possible equations are obtained:

$$\frac{x(b_1-a_1+x)}{a_1-x} = \frac{x(b_2-a_2+x)}{a_2-x}, \quad \dots \quad (4)$$

$$\frac{x(b_1-2a_1+x)}{a_1-x} = \frac{x(b_2-2a_2+x)}{a_2-x}, \quad \dots \quad (5)$$

$$\frac{x\left(\frac{b_1}{2}-a_1+x\right)^2}{a_1-x} = \frac{x\left(\frac{b_2}{2}-a_2+x\right)^2}{a_2-x}, \quad \dots \quad (6)$$

After substituting the values for a and b , it was found that, on solving the equations, only from (6) was a positive value for x

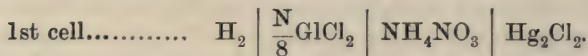
obtained. A similar result was obtained in the case of glucinum. Knowing the value of x , the magnitude of the hydrolysis constant can be found, from which it is then possible to calculate the amount of hydrolysis in a solution of sodium zincate or sodium glucinate of known concentration. It appears, therefore, that equation (3) correctly represents the hydrolysis of sodium zincate and sodium glucinate, and not equation (1), as stated by Hantzsch (*loc. cit.*). Sodium plumbite, as will be shown later, appears to behave in a different manner from the zinc and glucinum compounds, and to undergo hydrolysis more in agreement with Hantzsch's views.

EXPERIMENTAL.

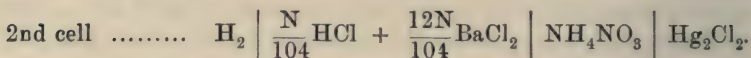
Glucinum Hydroxide Considered as a Base.

A sample of glucinum carbonate was obtained from Kahlbaum, and the quantity of oxide contained in it determined by Glassmann's method (*Ber.*, 1906, **39**, 3368). A weighed quantity of the carbonate was then dissolved in just sufficient of a solution of hydrochloric acid as was required to form the chloride, the proportions of glucinum and chlorine in the resulting solution being afterwards determined and compared, the former being estimated by Glassmann's and the latter by Volhard's method. A solution prepared as above and of $N/8$ -concentration with respect to chlorine was mixed with $1/200$ th of its volume of methyl formate, and the velocity of catalysis at 25° determined in the usual way. The mean value of the velocity constant was 0.00055. Comparison experiments were carried out with a solution of hydrochloric acid of $N/128$ -concentration, to which potassium chloride was added to bring the chlorine concentration up to $N/8$ (compare Walker and Wood, *Trans.*, 1903, **83**, 484); the mean result obtained for this solution was 0.00053. A comparison of these velocity constants shows that the fraction of the total chlorine existing in the condition of hydrochloric acid in a $N/8$ -solution of glucinum chloride is about 6.5 per cent. The amount of hydrolysis was also determined by the electromotive force method, the method of working being almost identical with that described by Beveridge (*Proc. Roy. Soc. Edin.*, 1909, **29**, 658). The only point of difference between Beveridge's experiments and those of the author was that barium chloride was added to the comparison solution containing hydrochloric acid. Barium chloride was chosen as being a salt of analogous composition to glucinum chloride, and it was added in sufficient quantity to bring the total chlorine concentration up to that in the glucinum chloride solution. The effect of this addition of barium chloride on the *E.M.F.* of the solution will be referred to later.

The following results were obtained :



Observed *E.M.F.* = 0.4076 volt.

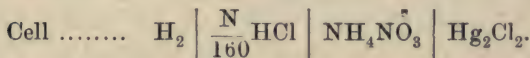


Observed *E.M.F.* = 0.3984 volt.

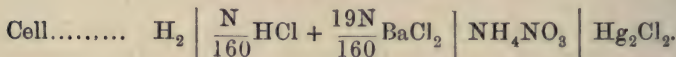
Difference in *E.M.F.* = 0.0092 volt.

By means of the formula $d = 0.0572 \log. \frac{c_1}{c_2}$ (Nernst, *Zeitsch. physikal. Chem.*, 1889, **4**, 129), it was calculated that in order that the comparison solution should have the same *E.M.F.* as that of the glucinum chloride, the concentration of hydrochloric acid should be $N/145$. Hence the hydrolysis = $8/145$, or 5.5 per cent. This result was confirmed by subsequent determinations. Solutions of glucinum chloride gave a constant hydrogen ion potential after they had been in the cell less than twenty-four hours; this is different from the behaviour observed by Denham (*Trans.*, 1908, **93**, 41) with solutions of salts of some other metals.

The addition of barium chloride or some other salt is of importance. If no such addition were made, the liquids in the two half-elements undergoing comparison would not be of a similar nature, one containing acid in presence of a large amount of salt, and the other acid only. The effect produced on the *E.M.F.* by the addition of barium chloride is shown by the following figures :



Observed *E.M.F.* = 0.4066 volt.



Observed *E.M.F.* = 0.4194 volt.

Difference caused by addition of BaCl_2 = 0.0128 volt.

The values obtained for the hydrolysis of glucinum chloride by the two methods are in fair agreement, the mean value being 6 per cent.; this figure is, however, greater than those previously obtained by Ley (*loc. cit.*) and Bruner (*loc. cit.*). The method already described for preparing the solutions of glucinum chloride is simple, and, with care, quite accurate. It is possible, however, that were insufficient care taken in standardising the hydrochloric acid or in

measuring the amount to be added to the glucinum carbonate, a solution might be obtained which contained a slight excess of acid; such a solution would, of course, appear to be more hydrolysed than one which contained so much excess. In order to test this point, a weighed quantity of glucinum sulphate was dissolved and mixed with a solution containing an equivalent amount of barium chloride. The barium sulphate was removed by filtration, and the concentration of the glucinum chloride forming the filtrate was then determined by analysis; it was found to be $0.35N$. This solution was mixed with methyl formate, a comparison experiment being conducted simultaneously with a $N/128$ -solution of hydrochloric acid containing barium chloride sufficient to bring the chloridion concentration to $0.35N$. The volume of the solution and the quantity of methyl formate being the same in both cases, the hydron concentration in the two solutions must be inversely proportional to the time necessary for the same amount of methyl formate to be hydrolysed. It was found that the reaction proceeded rather more rapidly in the solution containing glucinum chloride, the time necessary for the conversion of a certain quantity of ester being $21/23$ of that necessary in the other case. From this result it is obvious that a $0.35N$ -solution of glucinum chloride is hydrolysed to the extent of 2.44 per cent.

The various results were compared by calculating from each, as described in the earlier part of the paper, the amount of hydrolysis in a normal solution of glucinum chloride. The results obtained by the use of the solutions prepared from the carbonate gave a value of 2.2 per cent. for the hydrolysis in normal solution; the solution prepared from the sulphate gave a value of 1.45 per cent. It may be safely said, therefore, that a normal solution of glucinum chloride is hydrolysed to the extent of at least 1.5 per cent. at 25° .

Taking the above minimum value of 1.5 per cent., the hydrolysis constant of glucinum chloride is 0.000232, from which it follows that the weaker hydroxyl of glucinum hydroxide has a basic affinity of 5.2×10^{-11} .

Glucinum Hydroxide Considered as an Acid.

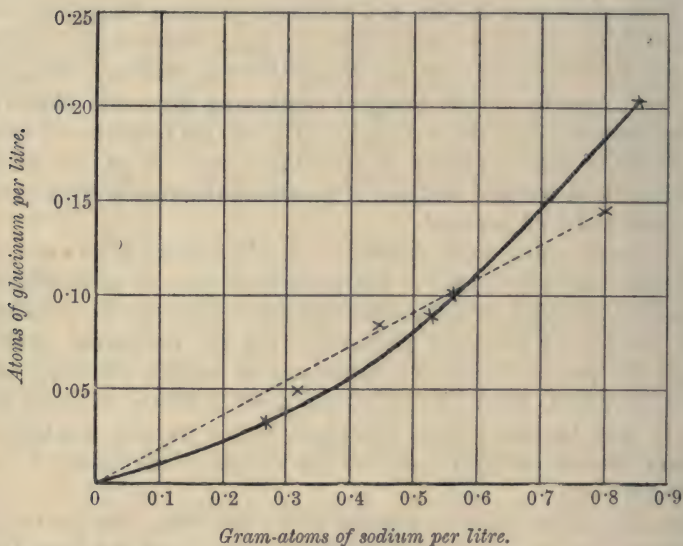
A solution of the chloride was prepared by dissolving glucinum carbonate in hydrochloric acid; from this the hydroxide was obtained by precipitation with ammonia, the product being repeatedly washed with warm distilled water. The solubility of the hydroxide in solutions of sodium hydroxide was then determined as described in the earlier part of the paper. The following results

were obtained, the figures representing the atomic concentrations of glucinum and sodium per litre:

	Glucinum.	Sodium.	Ratio Gl : Na.
A	0.0330	0.268	1 : 8.12
B	0.0492	0.318	1 : 6.47
C	0.0841	0.446	1 : 5.30
D	0.089	0.526	1 : 5.91
E	0.101	0.563	1 : 5.59
F	0.143	0.801	1 : 5.58
G	0.202	0.854	1 : 4.22

The above results differ slightly from those obtained by Haber and van Oordt (*loc. cit.*), the principal point of difference being that the ratio Gl : Na does not increase so rapidly with increase of con-

FIG. 1.



centration in the author's experiments as in those of Haber and van Oordt.

The curve representing the solubility of glucinum hydroxide in solutions of sodium hydroxide is shown in Fig. 1. It will be observed that this curve passes through the majority of the points experimentally determined, and also through the origin, as required by theory. Several of the points, in particular the one corresponding with solution F, do not fall on the curve. This discrepancy is rather too great to be the result of experimental error. It seems more probable that the cause must be sought for in the condition of the glucinum hydroxide. Haber and van Oordt (*loc. cit.*) showed

that the hydroxide changes in character, and that its solubility in solutions of alkali hydroxides diminishes when it has been kept at the ordinary temperature, heated in presence of water, etc. The glucinum hydroxide used by the author was freshly precipitated, and every precaution was taken to secure a uniform product; it is possible, however, that there may have been slight differences in character of the precipitate introduced into the various bottles along with the sodium hydroxide, and these differences, although slight, would probably be sufficient to explain results such as F. If a straight line be drawn joining F to the origin (shown by the dotted line in the figure), it will be observed that this line passes through E, and that B and C are also not far removed from it. It is possible, therefore, that the dotted line is also a solubility curve, showing the solubility of a different modification of glucinum hydroxide in solutions of sodium hydroxide. The following results, obtained by Haber and van Oordt, show that there is some justification for this view:

Millimol. Na per litre.	GlO (grams per litre).	Ratio Gl : Na.
649	3.6	1 : 4.5
540	2.92	1 : 4.6

The fact that the ratio Gl: Na remains almost unchanged in spite of a considerable change in the concentration shows that the solubility curve must approximate to a straight line. If the dotted line really does represent a solubility curve, it is obvious, from the difference between the two curves shown, that the salt in solution is not hydrolysed in the same manner in the two cases. The hydrolysis equation corresponding with the dotted line must be of the type of (1) or (2), the former being the more probable because of the weakness of the acid.

The hydrolysis constant has been calculated by means of equation (6) from the results A, D, E, and G. The mean value obtained was 0.00121, whence it follows that the amount of hydrolysis in a decinormal solution of sodium glucinate at 25° would be about 40 per cent. of the salt dissolved.

Zinc Hydroxide Considered as a Base.

Denham (*loc. cit.*) has already noticed the variation in hydron concentration, as measured by the electromotive force method, when solutions of zinc salts are examined from day to day. The author's experience was of a somewhat similar nature; some solutions when placed in the cell never attained equilibrium; others gave a definite value after several days, but in none of these cases were the values obtained in agreement with each other. It was therefore decided to use the catalysis method to estimate the amount of

hydrolysis in a solution of zinc chloride. The solution was prepared by mixing equivalent amounts of zinc sulphate and barium chloride and filtering off the precipitated barium sulphate, the concentration of the solution being then determined by analysis. The reaction with methyl formate being a very slow one, the action was not followed to its completion, but the times necessary for the same amount of ester to be hydrolysed by the zinc chloride solution and by the comparison solution were determined, and the hydrolysis then calculated as described in connexion with glucinum chloride. The solution of zinc chloride had a concentration of $0.53N$. The comparison solution consisted of a solution of hydrochloric acid having a concentration of $0.0031N$, to which barium chloride was added to make the chloridion concentration equal to that in the zinc chloride solution. It was found that the time necessary for these two solutions to hydrolyse equal amounts of methyl formate were in the ratio of 67 to 48. It may be said therefore that the free acid in the zinc chloride had a concentration of $\frac{48 \times 0.0031}{67} N$,

that is, $0.0022N$, which shows the hydrolysis of a $0.53N$ -solution of zinc chloride at 25° to amount to 0.4 per cent. This result is several times greater than that found by Ley (*loc. cit.*) for a much more dilute solution of zinc chloride, but it was confirmed by the results of other experiments.

The hydrolysis constant for zinc chloride calculated from the above figures is 8.4×10^{-6} , whence it follows that the weaker hydroxyl of zinc hydroxide must have a basic dissociation constant equal to 1.45×10^{-9} .

Zinc Hydroxide Considered as an Acid.

The zinc hydroxide necessary for the experiments was prepared by precipitation from zinc sulphate and sodium hydroxide. After thoroughly washing the product, it was mixed with solutions of sodium hydroxide, and the solubility determined as described in the first portion of the paper.

The following results were obtained, the numbers representing atoms of zinc and sodium per litre:

	Zinc.	Sodium.	Ratio Zn : Na.
A	0.00311	0.2636	1 : 84.7
B	0.0057	0.3871	1 : 67.9
C	0.0129	0.5414	1 : 42.0
D	0.0425	0.9280	1 : 21.8

It is evident from the figures in the last column and also from the solubility curve (Fig. 2) that the solubility of zinc hydroxide in solutions of sodium hydroxide varies much more with the con-

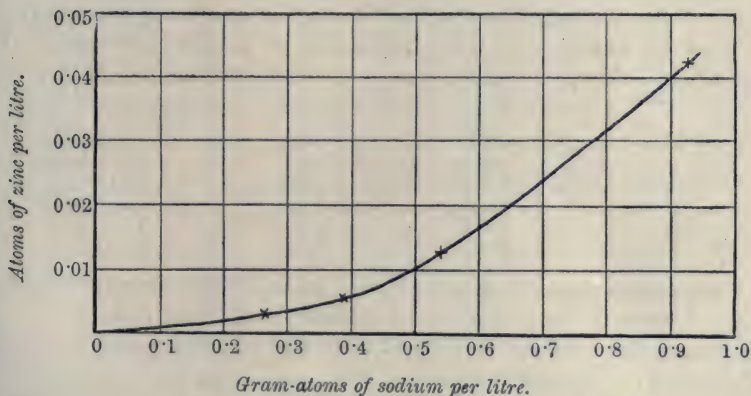
centration of the latter than does the solubility of glucinum hydroxide; this agrees with the observation of Rubenbauer (*loc. cit.*).

On calculating the solubility of zinc hydroxide in water from the above results, only one pair, namely, A and B, gave a positive value, the other pairs giving negative values of dimensions closely approaching zero. As equations (4) and (5) also failed to give positive values for x , the figure obtained from A and B, and having a magnitude of 0.00078, was taken as the solubility of zinc hydroxide in water. The hydrolysis constant corresponding with this value for x is 0.0056, from which it follows that the amount of hydrolysis in a decinormal solution of sodium zincate at 25° is 60 per cent.

Lead Hydroxide Considered as a Base.

For the investigation of the basic character of lead hydroxide the methyl formate catalysis method was found to be unsuitable,

FIG. 2.



owing to the indistinct nature of the end-point when the solution was titrated. The best results were obtained by using the method of Bredig and Fraenkel (*Ber.*, 1906, **39**, 1756), based on the decomposition of diazoacetic ester. As in some of the other determinations, the action was not carried to completion, but the time necessary for the evolution of the same volume of nitrogen, by the action of the two solutions undergoing comparison on equal amounts of diazoacetic ester, was determined.

Lead chloride was recrystallised from conductivity water and a solution prepared which had a concentration of 0.0575*N*. The comparison solution contained hydrochloric acid of concentration 0.00015*N*, to which potassium chloride was added to make the

chloridion concentration of the two solutions the same. Equal volumes of these solutions were mixed with equal quantities of diazoacetic ester solution, and the nitrogen evolved was collected in a measuring tube jacketed with water maintained at a constant temperature. With solutions having the concentration given above, the action in the two cases proceeded at the same rate, equal volumes of nitrogen being evolved in the same interval of time. A solution of lead chloride of concentration $0.0575N$ is therefore hydrolysed to the extent of 0.26 per cent. at 25° .

Calculating from this result, a decinormal solution of lead chloride would be hydrolysed to the extent of 0.2 per cent. at 25° , and the basic dissociation constant of the weaker hydroxyl has a value of 3.09×10^{-8} .

Lead Hydroxide Considered as an Acid.

The lead hydroxide was prepared by precipitating a solution of lead nitrate with ammonia and repeatedly washing the filtered product.

The following were the results obtained on analysing the solutions of lead hydroxide in various solutions of sodium hydroxide, the figures, as before, representing atomic concentrations per litre:

	Lead.	Sodium.	Ratio Pb : Na.
<i>A</i>	0.0181	0.274	1 : 15.11
<i>B</i>	0.0287	0.431	1 : 15.02
<i>C</i>	0.0318	0.476	1 : 14.97
<i>D</i>	0.0489	0.745	1 : 15.24
<i>E</i>	0.0711	1.132	1 : 15.92
<i>F</i>	0.101	1.519	1 : 15.04

The most striking feature of these results is the constancy of the ratio between the amounts of sodium and lead present in the solutions, from which it follows that the solubility curve of lead hydroxide in solutions of sodium hydroxide must be a straight line (Fig. 3). If the three possible expressions for the hydrolysis constant, given in the earlier part of the paper, are considered, and if it be remembered that x has a constant value of very small dimensions, it will be seen that only the first and second expressions can represent a straight line, as the third expression involves higher powers than the first of the variables a and b . It would seem, therefore, that the hydrolysis of sodium plumbite proceeds in a manner different from that of sodium zincate, and that the hydrolysis constant must be calculated by means of equation (4) or (5) instead of by equation (6). Taking into account the weakness of the acid, it is probable that equation (4) is the correct one to employ. Making use of this equation the hydrolysis constant is found to have the value 0.0035. The amount of hydrolysis in a

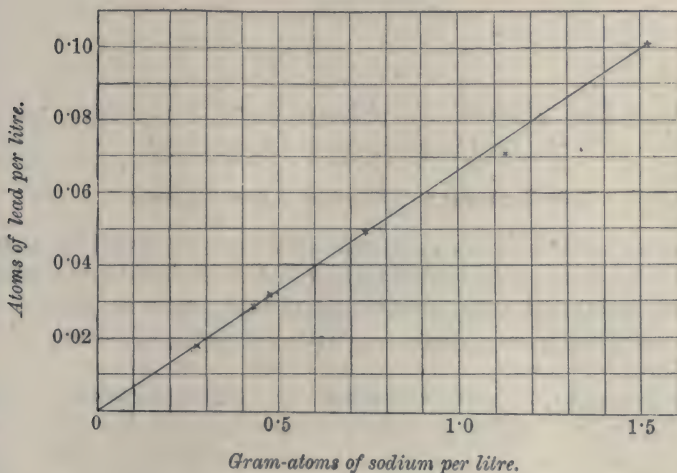
decinormal solution of sodium plumbite, calculated from the above value for the hydrolysis constant, is equal to 17 per cent.

Summary of Results and Conclusions.

	Hydrolysis of $N/10$ - solution of chloride.	K_b of weaker hydroxyl of hydroxide.	Hydrolysis of $N/10$ - solution of sodium salt of hydroxide.
Glucinum	4.6 per cent.	5.2×10^{-11}	40 per cent.
Zinc	0.9 „	145.0×10^{-11}	60 „
Lead	0.2 „	3090.0×10^{-11}	17 „

From the above table it is seen that lead hydroxide is the strongest, and glucinum hydroxide the weakest base. Strictly speaking, this only refers to the weaker hydroxyl of each compound, but it is

FIG. 3.



probable that if the basic strength of the other hydroxyl could be determined, the same order would be observed. It must be noted that the order of basicity found by the author differs from that arrived at by Ley (*loc. cit.*), who found zinc hydroxide to be the strongest, and glucinum hydroxide the weakest base. A certain amount of support in favour of the position occupied by lead hydroxide, according to the results of the author's experiments, is the well-known fact that aqueous solutions of lead hydroxide have an alkaline reaction towards litmus; this, however, is not a positive proof of the correctness of the result, for the concentration of hydroxidion depends not only on the degree of ionisation, but also on the amount of hydroxide in solution.

The order of acidity of the hydroxides, as determined by the

author, is identical with that arrived at by other methods by Hantzsch (*loc. cit.*); as the sodium compound of lead hydroxide is the least hydrolysed and that of zinc hydroxide the most hydrolysed, lead hydroxide is obviously the strongest, and zinc hydroxide the weakest acid.

The salt present in solution has the formula assigned by Hantzsch, namely, $\text{Pb}(\text{OH})\text{ONa}$ in the case of lead, but in the case of zinc the evidence of the author's experiments points to the salt having the formula $\text{Zn}(\text{ONa})_2$. As regards glucinum, a salt of the formula $\text{Gl}(\text{ONa})_2$ exists in solution, and possibly also one having the formula $\text{Gl}(\text{OH})\text{ONa}$.

UNIVERSITY COLLEGE,
DUNDEE.

LXIV.—*The Action of Phosphorus Pentachloride on Some Unsaturated Compounds.*

By REGINALD WILLIAM LANE CLARKE.

THE subject of the present communication was suggested by a study of the behaviour of piperonylacrylic (3:4-methylenedioxy-cinnamic) acid on treatment with phosphorus pentachloride at higher temperatures than those usually employed for the preparation of acid chlorides.

The behaviour of methylene ethers of catechol on treatment with phosphorus pentachloride has been investigated by Fittig and Remsen (*Annalen*, 1871, **159**, 144), more recently by Pauly (*Ber.*, 1907, **40**, 3096) and Barger (*Trans.*, 1908, **93**, 563). The results described hereafter confirm the conclusions drawn by Barger (*loc. cit.*) as regards the replacement of the two methylene hydrogen atoms by chlorine, and also the reactivity of those chlorine atoms. This case was, however, further complicated owing to the unsaturated nature of the acid.

It was found that when piperonylacrylic acid was treated with phosphorus pentachloride, a substance, $\alpha\beta$ -dichloro-3:4-dichloro-methylenedioxy- β -phenylpropionyl chloride,

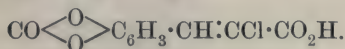


containing five chlorine atoms, was produced, showing that the doubly linked carbon atoms had been saturated by chlorine, and

also that the expected displacement had occurred. This substance reacts vigorously with anhydrous formic acid, giving *αβ-dichloro-3: 4-carbonyldioxy-β-phenylpropionic acid*,

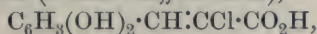


On boiling with formic acid, however, this loses hydrogen chloride, giving *α-chloro-3: 4-carbonyldioxy-cinnamic acid*,



The *α*-position is assigned to the chlorine atom on account of the behaviour of the analogous dichlorides and dibromides of cinnamic acid, which, on treatment with alkalis, give *α-chloro-* or *α-bromo-*cinnamic acid.

When *α-chloro-3: 4-carbonyldioxy-cinnamic acid* is boiled with water, the carbonyl group is eliminated, and *α-chloro-3: 4-dihydroxycinnamic acid (α-chlorocaffeic acid)*,



is produced.

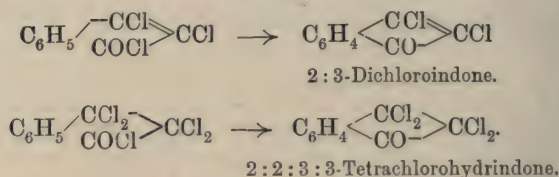
In view of the behaviour of this unsaturated acid with phosphorus pentachloride, it was thought desirable to investigate the behaviour of other unsaturated substances with that reagent under similar conditions. A number of substances containing an ethenoid linking was employed, also one substance, namely, phenylpropionic acid, containing an acetylenic linking. In all cases it was found that the addition of chlorine to the unsaturated carbon atoms took place, as well as the usual reactions which the compound undergoes on treatment with phosphorus pentachloride at lower temperatures.

Thus cinnamic acid gives *αβ-dichloro-β-phenylpropionyl chloride*, $\text{CHPhCl} \cdot \text{CHCl} \cdot \text{COCl}$, and from it the corresponding acid and esters can easily be prepared.

α-Chlorocinnamic acid yields *ααβ-trichloro-β-phenylpropionyl chloride*, $\text{CHPhCl} \cdot \text{CCl}_2 \cdot \text{COCl}$, which gives *ααβ-trichloro-β-phenylpropionic acid*, $\text{CHPhCl} \cdot \text{CCl}_2 \cdot \text{CO}_2\text{H}$, on suitable treatment. This acid loses hydrogen chloride readily, giving the *αβ-dichlorocinnamic acid*, obtained by chlorinating phenylpropionic acid in chloroform solution (Nissen, *Ber.*, 1892, **25**, 2665).

Phenylpropionic acid, on treatment with phosphorus pentachloride at 200°, yields *αβ-dichlorocinnamyl chloride*, and at the same time 2: 3-dichloroindone and 2: 2: 3: 3-tetrachlorohydrindone—a rather curious behaviour, inasmuch as the formation of these bicyclic compounds can only be accounted for by the elimination of hydrogen chloride from the corresponding acid chlorides, as there is no doubt that the first product of the reaction between phenyl-

propionic acid and phosphorus pentachloride is phenylpropionyl chloride:



This reaction furnishes an easy method by which these substances can be produced.

This behaviour with phosphorus pentachloride is not confined to substances which contain a benzene nucleus. Crotonic acid, on heating with phosphorus pentachloride, gives $\alpha\beta$ -dichlorobutyryl chloride, which has been obtained by Zeisel (*Monatsh.*, 1888, **7**, 360) by treating crotonaldehyde with chlorine. The constitution of this substance was proved by converting it into $\alpha\beta$ -dichlorobutyric acid.

The action of phosphorus pentachloride on cinnamaldehyde was also investigated, and $\alpha\beta\gamma\gamma$ -tetrachloro- α -phenylpropane, $\text{CHPhCl}\cdot\text{CHCl}\cdot\text{CHCl}_2$, was isolated, which has the same composition as the substance obtained by Charon and Dugoujon (*Compt. rend.*, 1903, **136**, 94), by treating cinnamaldehyde with phosphorus pentachloride at the ordinary temperature, thereby obtaining cinnamylidene chloride, and subsequently treating this product with chlorine. The substance obtained by the direct treatment of cinnamaldehyde with phosphorus pentachloride melts at 98° , whereas Charon and Dugoujon give the melting point of the substance isolated by them as 66° ; the difference in properties may possibly be explained on stereoisomeric grounds.

EXPERIMENTAL.

Action of Phosphorus Pentachloride on Cinnamic Acid.

Formation of $\alpha\beta$ -Dichloro- β -phenylpropionyl Chloride, $\text{CHPhCl}\cdot\text{CHCl}\cdot\text{COCl}$.

Fifty grams of cinnamic acid were heated with 143 grams of phosphorus pentachloride at 180° for two hours under an air condenser; the phosphorus chlorides were removed by heating to 110° in a vacuum; the residue was then distilled under diminished pressure, when nearly all passed over at $133\text{--}136^\circ/14$ mm. The product was redistilled, and 81 grams of a yellow oil, boiling at $134\text{--}136^\circ/14$ mm., were obtained; the oil solidified on cooling, and a portion was purified for analysis by repeated crystallisation from light petroleum:

0.221 gave 0.3682 CO_2 and 0.0602 H_2O . $\text{C}=45.4$; $\text{H}=3.03$.

0.1574 „ 0.2854 AgCl . $\text{Cl}=44.8$.

$\text{C}_9\text{H}_7\text{OCl}_3$ requires $\text{C}=45.5$; $\text{H}=2.95$; $\text{Cl}=44.8$ per cent.

$\alpha\beta$ -Dichloro- β -phenylpropionyl chloride is readily soluble in benzene, ether, or light petroleum, and crystallises from the latter solvent in small, flattened needles, which melt at 55° and boil at $136^\circ/14$ mm. It is only very slowly attacked by cold water; when heated on the water-bath for two hours with water or anhydrous formic acid, it yields *$\alpha\beta$ -dichloro- β -phenylpropionic acid*, which, after crystallisation from chloroform, melts at 167° .

$\alpha\beta$ -Dichloro- β -phenylpropionyl chloride gave, on treatment with methyl alcohol, the corresponding methyl ester (m. p. 100 — 101°), which agreed in properties with methyl *$\alpha\beta$ -dichloro- β -phenylpropionate* described by Finkenbeiner (*Ber.*, 1894, **27**, 890).

Action of Phosphorus Pentachloride on α -Chlorocinnamic Acid.

$\alpha\alpha\beta$ -Trichloro- β -phenylpropionyl Chloride, $\text{CHPhCl}\cdot\text{CCl}_2\cdot\text{COCl}$.

α -Chlorocinnamic acid (10 grams), prepared by heating *$\alpha\beta$ -dichloro- β -phenylpropionyl chloride* with aqueous potassium hydroxide (compare Erlenmeyer, *Ber.*, 1881, **14**, 1867; Jutz, *ibid.*, 1882, **15**, 788; Michael and Pendleton, *J. pr. Chem.*, 1889, [ii], **40**, 63), was heated with phosphorus pentachloride (25 grams: 2 mols.) for three and a-half hours at 200° . The chlorides of phosphorus were removed by heating in a vacuum at 125 — 130° , and the residue was fractionated under diminished pressure, when 7.2 grams of oil boiling at 143 — $145^\circ/14$ mm. (first fraction), and 3.3 grams of oil boiling at 149 — $151^\circ/14$ mm. (second fraction) were obtained.

Each fraction was found to consist of *$\alpha\alpha\beta$ -trichloro- β -phenylpropionyl chloride*, the second fraction being rather purer than the first:

0.323 gave 0.674 AgCl . $\text{Cl}=51.7$.

$\text{C}_9\text{H}_6\text{OCl}_4$ requires $\text{Cl}=52.2$ per cent.

$\alpha\alpha\beta$ -Trichloro- β -phenylpropionyl chloride is a yellow oil with a pungent, aromatic odour, and does not solidify when cooled to -10° . It is miscible with benzene, ether, chloroform, or light petroleum, but not with water, and reacts very slowly with water or aqueous alkalis at the ordinary temperature. On heating on the water-bath with water, aqueous sodium hydroxide, or anhydrous formic acid, it yields the unsaturated dichlorocinnamic acid.

$\alpha\alpha\beta$ -Trichloro- β -phenylpropionic Acid, $\text{CHPhCl}\cdot\text{CCl}_2\cdot\text{CO}_2\text{H}$.

This substance was prepared from the corresponding acid chloride by treating it with pyridine in benzene solution at the ordinary

temperature. The benzene solution was shaken with dilute hydrochloric acid to remove the pyridine, and the benzene layer was then extracted with dilute aqueous sodium carbonate; on acidification this yielded an oily acid, which soon solidified, and was purified by crystallisation from light petroleum or carbon tetrachloride:

0.2002 gave 0.3125 CO_2 and 0.0540 H_2O . $\text{C}=42.5$; $\text{H}=2.99$.

0.1336 „ 0.2294 AgCl . $\text{Cl}=42.4$.

$\text{C}_9\text{H}_7\text{O}_2\text{Cl}_3$ requires $\text{C}=42.6$; $\text{H}=2.76$; $\text{Cl}=42.0$ per cent.

This acid is very soluble in benzene, ethyl acetate, or chloroform, sparingly so in light petroleum, and crystallises from carbon tetrachloride in rectangular plates, which melt at 115° . It was also obtained by exposing the corresponding acid chloride to moist air, also by dissolving it in acetone and adding a small quantity of water, evaporating the acetone at the ordinary temperature under diminished pressure, rendering the liquid alkaline with sodium carbonate, and extracting with ether to remove neutral material. The alkaline liquid, on acidifying, gave an acid which, after crystallisation from a mixture of chloroform and light petroleum, melted at 115° . The identity of this substance with that obtained by the pyridine treatment was established by the mixed melting-point method.

Preparation of $\alpha\beta$ -Dichlorocinnamic Acid.

$\alpha\alpha\beta$ -Trichloro- β -phenylpropionyl chloride (3 grams) was added to a solution of potassium hydroxide (2 grams) in 10 c.c. of water, and sufficient alcohol added to render the liquid clear. The mixture was then heated on the water-bath for one hour, and the alcohol and neutral volatile material removed by a current of steam. The distillate was extracted with ether, and gave, after the usual treatment, a small quantity of oil boiling at 220 — 223° under the ordinary pressure. The residual liquid was then acidified, and the acid which separated was crystallised from a mixture of chloroform and light petroleum. (Found, $\text{C}=49.2$; $\text{H}=2.86$; $\text{Cl}=32.9$. Calc., $\text{C}=49.7$; $\text{H}=2.76$; $\text{Cl}=32.7$ per cent.)

The acid crystallised from chloroform or light petroleum in prismatic needles, melting at 123° , and is evidently identical with the $\alpha\beta$ -dichlorocinnamic acid described by Nissen (*Ber.*, 1892, **25**, 2665). The same acid was also produced when $\alpha\alpha\beta$ -trichloro- β -phenylpropionyl chloride was warmed on the water-bath with anhydrous formic acid.

Methyl $\alpha\beta$ -Trichloro- β -phenylpropionate, $\text{CHPhCl}\cdot\text{CCl}_2\cdot\text{CO}_2\text{Me}$.

For the preparation of this ester, $\alpha\beta$ -trichloro- β -phenylpropionyl chloride (second fraction, b. p. $149\text{--}151^\circ/14$ mm.) was mixed with twice its volume of methyl alcohol. On cooling a crystalline substance separated, which was collected, washed with methyl alcohol, and recrystallised three times from the same solvent, separating from it in colourless, flat, rectangular prisms, melting at 66° :

0.2016 gave 0.3274 CO_2 and 0.0608 H_2O . $\text{C}=44.3$; $\text{H}=3.36$.

0.1406 „ 0.2252 AgCl . $\text{Cl}=39.6$.

$\text{C}_{10}\text{H}_9\text{O}_2\text{Cl}_3$ requires $\text{C}=44.9$; $\text{H}=3.37$; $\text{Cl}=39.7$ per cent.

Action of Phosphorus Pentachloride on Phenylpropionic Acid.

Phenylpropionic acid (10 grams) was mixed with phosphorus pentachloride (44 grams: 3 mols.), and, after the first reaction had subsided, the mixture was heated at $200\text{--}210^\circ$ under an air condenser for four hours. The phosphorus chlorides were removed by heating in a vacuum at 120° . The residue was then rapidly distilled in a vacuum, and the distillate fractionated under diminished pressure. The first distillation was necessary, as much frothing occurred.

Fraction 1, $127\text{--}137^\circ/14$ mm., consisted of $\alpha\beta$ -dichlorocinnamyl chloride mixed with some 2:3-dichloroindone, which crystallised out after some time. The oil was poured off from the crystals, and on treatment with anhydrous formic acid furnished $\alpha\beta$ -dichlorocinnamic acid (m. p. 123°) identical with the acid described above (p. 894).

Fraction 2, $138\text{--}145^\circ/14$ mm., which solidified in the receiver, was drained on porous porcelain, and consisted of bright orange-coloured needles, which were crystallised several times from light petroleum. (Found, $\text{C}=53.9$; $\text{H}=2.08$; $\text{Cl}=35.8$. Calc., $\text{C}=54.3$; $\text{H}=2.01$; $\text{Cl}=35.7$ per cent.)

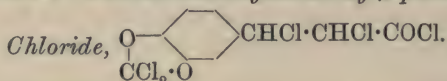
The substance melted at $87\text{--}88^\circ$, and its properties showed it to be identical with 2:3-dichloroindone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CCl} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CCl}$ (Roser and Haselhoff, *Annalen*, 1888, **247**, 151).

Fraction 3, $158\text{--}161^\circ/14$ mm., which also solidified in the receiver, was found to consist chiefly of 2:2:3:3-tetrachlorohydrindone, $\text{C}_6\text{H}_4\begin{smallmatrix} \text{CCl}_2 \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} \text{CCl}_2$ Zincke and Fröhlich, *Ber.*, 1887, **20**, 2053), together with a small quantity of dichloroindone, from which it was separated by fractional crystallisation from light petroleum, in which solvent the tetrachlorohydrindone is less soluble.

This substance was obtained in long, colourless, prismatic needles, which melted at 105° (Found, $C=40.0$; $H=1.68$; $Cl=52.4$. Calc., $C=40.0$; $H=1.48$; $Cl=52.6$ per cent.)

Action of Phosphorus Pentachloride on Piperonylacrylic Acid.

$\alpha\beta$ -Dichloro-3: 4-dichloromethylenedioxy- β -phenylpropionyl



The piperonylacrylic acid was prepared by condensing piperonal with ethyl acetate in presence of sodium, and subsequently hydrolysing the ester produced with aqueous potassium hydroxide (compare Perkin and Robinson, *Trans.*, 1907, **91**, 1079).

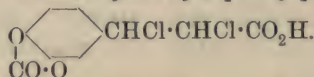
Piperonylacrylic acid (20 grams) was mixed with phosphorus pentachloride (90 grams: 4 mols.), and the mixture heated at 160 — 170° for four to five hours. The chlorides of phosphorus were removed by heating in a vacuum, and the product was distilled under diminished pressure. After several distillations, a light brown, viscid oil was obtained, which boiled at $194^{\circ}/8$ mm., or $202^{\circ}/15$ mm.:

0.1830 gave 0.3594 AgCl. $Cl=48.6$.

$C_{10}H_5O_3Cl_5$ requires $Cl=50.7$ per cent.

This acid chloride is rapidly affected by exposure to atmospheric moisture; it reacts vigorously with water or anhydrous formic acid, losing chlorine from the acid chloride ($COCl$) group and also from the chloromethylene group.

$\alpha\beta$ -Dichloro-3: 4-carbonyldioxy- β -phenylpropionic Acid,

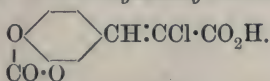


When formic acid is added to $\alpha\beta$ -dichloro-3: 4-dichloromethylenedioxy- β -phenylpropionyl chloride, a vigorous reaction ensues; hydrogen chloride is evolved, and $\alpha\beta$ -dichloro-3: 4-carbonyldioxyphenylpropionic acid separates. The pasty mass was drained, washed with anhydrous formic acid, and finally with light petroleum, and dried on porous porcelain in a vacuum desiccator:

0.1069 gave 0.1122 AgCl. $Cl=25.9$.

$C_{10}H_6O_5Cl_2$ requires $Cl=25.6$ per cent.

This compound is unstable; on heating with anhydrous formic acid or on exposure to moist air, it loses hydrogen chloride, giving the corresponding unsaturated acid.

α -Chloro-3: 4-carbonyldioxy cinnamic Acid,

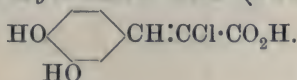
This acid, prepared from the preceding one by boiling it with anhydrous formic acid, separates from the liquid on cooling; it was purified by crystallisation from anhydrous formic acid:

0.1378 gave 0.2526 CO_2 and 0.0279 H_2O . $\text{C}=50.0$; $\text{H}=2.25$.

0.1325 „ 0.0827 AgCl . $\text{Cl}=15.4$.

$\text{C}_{10}\text{H}_5\text{O}_5\text{Cl}$ requires $\text{C}=49.9$; $\text{H}=2.08$; $\text{Cl}=14.8$ per cent.

The compound melts at 241° , and sublimes unchanged at $240^\circ/11 \text{ mm.}$, condensing in small needles. It is sparingly soluble in ethyl acetate, benzene, or chloroform, insoluble in light petroleum, but soluble in hot acetic or formic acids. When boiled with water the cyclic carbonate ring is ruptured, and the corresponding catechol derivative is produced. This substance can, however, be more directly prepared as described below.

 α -Chloro-3: 4-dihydroxycinnamic Acid (α -Chlorocaffeic Acid),

This substance was obtained directly from $\alpha\beta$ -dichloro-3: 4-dichloromethylenedioxy- β -phenylpropionyl chloride by heating with about five times its weight of acetone and an equal quantity of water on the water-bath, and adding powdered marble to neutralise the hydrochloric acid liberated. When the effervescence had ceased, the acetone was distilled off, and the residual liquid extracted with ether. After removing the ether, the residue solidified, and was crystallised several times from formic acid and finally from water:

0.1538 gave 0.2834 CO_2 and 0.0475 H_2O . $\text{C}=50.25$; $\text{H}=3.43$.

0.1004 „ 0.0680 AgCl . $\text{Cl}=16.7$.

$\text{C}_9\text{H}_7\text{O}_4\text{Cl}$ requires $\text{C}=50.35$; $\text{H}=3.27$; $\text{Cl}=16.5$ per cent.

α -Chloro-3: 4-dihydroxycinnamic acid separates from water in small, colourless, flattened prisms, which melt and darken at $207\text{--}208^\circ$. Its aqueous solution gives, with ferric chloride, a dark green colour, turned red by alkalis, a reaction characteristic of catechol derivatives. It is almost insoluble in benzene, toluene, or light petroleum, but fairly soluble in ethyl acetate.

Action of Phosphorus Pentachloride on Crotonic Acid.

Crotonic acid (3 grams) was heated to 160° for two hours with phosphorus pentachloride (2 mols.: 16 grams), and the product was fractionally distilled under the ordinary pressure (765 mm.). The fraction of highest boiling point, $166\text{--}170^{\circ}$, was collected separately, and consisted of a colourless oil, possessing a pungent odour. (Found, $\text{Cl}=62.3$. Calc., $\text{Cl}=60.7$ per cent.)

The high value found for chlorine is probably due to the presence of a small amount of phosphorus pentachloride or trichloride. The substance is evidently identical with the $\alpha\beta$ -dichlorobutyryl chloride obtained by Zeisel (*Monatsh.*, 1888, **7**, 360) by treatment of crotonaldehyde with chlorine.

The acid chloride was converted into the corresponding $\alpha\beta$ -dichlorobutyric acid by agitation with sodium hydrogen carbonate solution until the oil had disappeared. The liquid was then acidified with hydrochloric acid, and extracted with ether. The residue, after removing the ether, was distilled under diminished pressure; it boiled at $120^{\circ}/13$ mm., and solidified in the receiver on cooling. It was purified by crystallisation from light petroleum, from which it separated in colourless crystals, melting at $62\text{--}63^{\circ}$. (Found, $\text{Cl}=45.6$. Calc., $\text{Cl}=45.2$ per cent.)

The properties of the substance indicate that it is $\alpha\beta$ -dichlorobutyric acid (compare Zeisel, *loc cit.*).

*Action of Phosphorus Pentachloride on Cinnamaldehyde.**Preparation of $\alpha\beta\gamma\gamma$ -Tetrachloro- α -phenylpropane,
 $\text{CHPhCl}\cdot\text{CHCl}\cdot\text{CHCl}_2$.*

Phosphorus pentachloride (33 grams: 2 mols.) was added to well-cooled cinnamaldehyde (10 grams) in small quantities at a time; a vigorous reaction ensued, which was accompanied by a series of colour changes; the mixture was then heated for five hours at $110\text{--}120^{\circ}$, after removal of the phosphorus chlorides by heating in a vacuum; the residue was distilled, when 12 grams of oil boiling at $157\text{--}163^{\circ}/15$ mm., which solidified in the receiver, were obtained. It was purified by crystallisation from light petroleum, from which it separated in colourless, prismatic needles, melting at $99\text{--}100^{\circ}$:

0.1628 gave 0.2490 CO_2 and 0.0460 H_2O . $\text{C}=41.7$; $\text{H}=3.14$.

0.1392 „ 0.3102 AgCl . $\text{Cl}=55.1$.

$\text{C}_9\text{H}_8\text{Cl}_4$ requires $\text{C}=41.8$; $\text{H}=3.10$; $\text{Cl}=55.0$ per cent.

The substance is fairly stable; it was recovered unchanged after heating with water or anhydrous formic acid for some time. It is moderately volatile in steam.

Charon and Dugoujon (*Compt. rend.*, 1903, **136**, 94) describe a substance to which they assign the formula $\text{CHPhCl} \cdot \text{CHCl} \cdot \text{CHCl}_2$, obtained by treating cinnamaldehyde with (1 mol.) phosphorus pentachloride, and subjecting the resulting cinnamylidene chloride to the action of chlorine. In this way they obtained a substance, $\text{C}_9\text{H}_8\text{Cl}_4$, melting at 66° , that is, $33\text{--}34^\circ$ lower than the melting point of the substance just described.

In conclusion, the author desires to thank Dr. Barger for encouragement and advice.

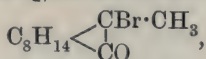
GOLDSMITHS' COLLEGE,
NEW CROSS.

LXV.—*Studies of Dynamic Isomerism. Part X.*
The Relationship between Absorption Spectra and
Isomeric Change. Absorption Spectra of Camphor-
carboxylic Acid and its Derivatives.

By THOMAS MARTIN LOWRY, CECIL HENRY DESCH, and
HERBERT WILLIAM SOUTHGATE.

IN two previous papers (Lowry and Desch, *Trans.*, 1909, **95**, 807, 1340) evidence was brought forward in reference to the absorption spectra of a number of derivatives of camphor, which were examined for the specific purpose of determining whether the development of absorption bands was or was not related to the occurrence of reversible isomeric change in their solutions.

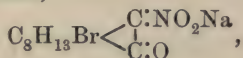
Two chief series of compounds were examined. In the one series—including camphor itself and many of its simpler derivatives—a shallow band was found at $1/\lambda$ 3350 to 3500. As this band was developed by neutral and acid solutions of substances, such as α -bromocamphor, which undergo isomeric change only in presence of alkalis, it was evidently not dependent on these changes; final confirmation of this opinion was derived from the discovery that a shallow band exists in the spectrum of α -bromo- α' -methylcamphor,



a substance in which isomeric change is rendered impossible by the elimination of the mobile hydrogen atom. The conclusion was therefore arrived at that the band is in some way a specific property of the carbonyl group, its intensity being influenced by the character of the adjacent atoms in a way that has become familiar from the

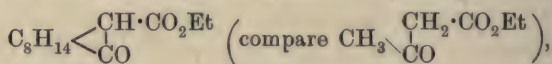
study of the related phenomena of refraction, dispersion, and magnetic rotation.

In the second series a very deep band was observed at $1/\lambda$ 3100 in the spectrum of the sodium salt of nitrocamphor. This band was not developed by the nitro-compound itself, although it undergoes isomeric change with the utmost readiness, nor by any of its derivatives except the salts,

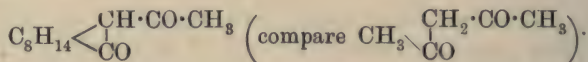


of the β - and π -bromonitro-compounds, which contain the same characteristic grouping of atoms as the sodium salt from which they are derived. In this series, also, the absorption band appeared to be in no way related to the occurrence of isomeric change, and was attributed to the presence in the salts of a system of conjugated double bonds which was absent from the formulæ of the other compounds of the series.

Although the evidence thus obtained was sufficiently conclusive in regard to the main problem, the compounds examined differed somewhat widely in character from those on which Baly and Desch had based their hypothesis, and it was therefore thought desirable to extend the observations to the analogous derivatives of camphor. The compounds corresponding most closely with ethyl acetoacetate and acetylacetone are ethyl camphorcarboxylate:



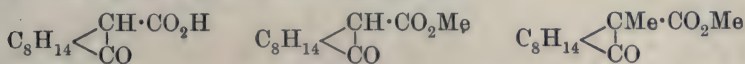
and acetylcamphor:



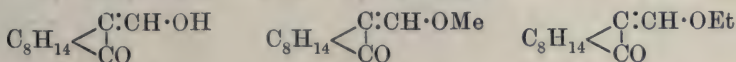
Both of these compounds, as well as a large number of their derivatives, have been exhaustively studied by Brühl, who has made a detailed examination of their refractive and dispersive powers (*Ber.*, 1902, **35**, 3510, *et seq.*), with the result that much information was already available in reference to their actual molecular configuration. Prof. Brühl was kind enough to place at our disposal his valuable series of specimens, and much of the success of the present investigation is due to his generosity in this matter. We were also fortunate enough to secure the use of two crystalline derivatives of camphorcarboxylic acid—an amide and a piperidide—which had been prepared by Dr. Glover and found to undergo isomeric change in solution. To both of the above we desire to tender our thanks.

The experimental methods were identical with those previously described. The increased dispersion secured by the use of a four half-prism system, combined with an increase in the time of exposure, was found to be of the utmost value in the case of substances producing shallow or doubtful bands; the labour of plotting the curves was much reduced by the logarithmic graduation of the tube containing the solutions and by the use of a standard plate ruled right across (by cutting the film with a penknife) in exact multiples of 50 units of frequency.

The new observations provided further evidence that the bands were not due to isomeric change, since curves of precisely similar form were given by the three compounds:



in spite of the fact that the first *does* not, and the third *can* not undergo isomeric change in solution. Again, spectra of exactly the same type, each showing a strong absorption band, are given by hydroxymethylenecamphor and by its methyl and ethyl ethers:



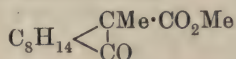
in spite of the fact that only the first undergoes isomeric change in solution, or is affected by the addition of alkali. These results were perhaps only to be expected in view of the observations recorded in the preceding papers of the series, but the evidence is now so conclusive (applying, as it does, both to the deep and to the shallow bands) that the matter may be regarded as finally settled and need not be referred to again. Instead, an attempt will be made, in the paper immediately following, to develop on a constructive basis a theory as to the origin of the bands, to take the place of the earlier views, which are now known to be untenable.

The derivatives of camphorcarboxylic acid may be divided into four chief groups, according to their absorption curves, namely:

(1) The *normal* series of compounds, including (a) the acid, (b) its sodium salt, (c) the methyl, ethyl, and amyl esters, (d) the amide and piperidide, and, finally, (e) the methyl ester of methylcamphorcarboxylic acid.

Each of these compounds gives a shallow band at $1/\lambda$ 3450, the head of the band being reached at a thickness of some 100 mm. of $N/100$ -solution. The band is similar in position, and occurs at a concentration similar to that observed in the case of camphor itself; we believe, therefore, that it may be attributed to the carbonyl group of the camphor, and that the groups $\cdot\text{CO}\cdot\text{OH}$, $\cdot\text{CO}\cdot\text{ONa}$, $\cdot\text{CO}\cdot\text{OEt}$, $\cdot\text{CO}\cdot\text{NH}_2$, etc., are without substantial influence on the

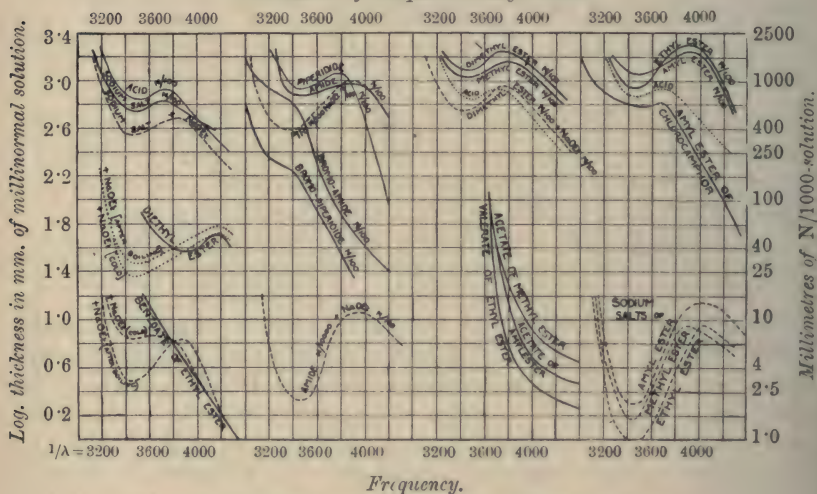
absorptive properties of the ketone. The actual chemical constitution of this group of compounds follows from that of the dimethyl ester, to which the formula



must obviously be assigned, as it is the parent substance from which methylcamphor, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{CHMe} \\ | \\ \text{CO} \end{array}$, is prepared.

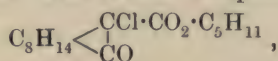
(2) The *halogen* derivatives. The compounds examined were the

Derivatives of camphorcarboxylic acid.



Curves for alkaline solutions are drawn with broken lines.

chloro-derivative of the amyl ester and the bromo-derivatives of the amide and piperidide. The former compound,



showed, at a thickness of 60 mm. of *N*/100-solution, a horizontal extension of the spectrum, which might be read alternatively as a shallow band with its head at $1/\lambda$ 3500. The alteration in the spectrum is here very slight, consisting only of a small increase of general absorption coupled with a small decrease in the local or specific absorption. In the two bromo-compounds:



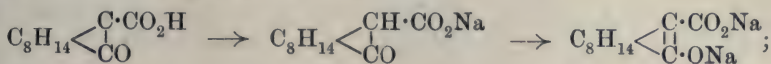
the effects produced by the halogen atom are (as is usual) greater; the general absorption is much increased, and, although each curve

runs out somewhat rapidly at $1/\lambda$ 3200, there is no horizontal part in either curve.

(3) The *enolic* salts. The addition of alkali to the esters of camphorcarboxylic acid produces an enormous increase of absorptive power, the head of the band being extended from 100 mm. of $N/100$ -solution to 25—10 mm. of a solution one hundred times more dilute, a change which represents an increase of absorptive power in the ratio of 250—1000 to 1; as regards frequency, the head of the band remains, as in the parent substances, at $1/\lambda$ 3450. This fundamental change in the absorption spectrum does not take place in the case of the dimethyl ester, and is evidently due to the formation of an enolic sodium salt:



The acid itself does not behave in this way, the spectrum being practically unaffected by the addition of 1 or of 9 equivalents of alkali. So far as mere formulæ are concerned there is no obstacle to the formation of an enolic disodium salt:



but it is well known from the study of polybasic acids that the readiness with which the acidic hydrogen atoms are displaced decreases as atom after atom of metal is introduced into the molecule, and there can be little doubt that similar considerations apply in the present case; the feeble acidic properties of the enolic esters would thus be reduced to zero by the introduction of the first sodium atom, and no formation of a disodium salt could then take place.

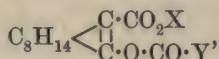
The contrast which is thus revealed between the esters and the acid appears again in the case of the amide and piperidide. The former compound, when acted on by alkalis, gives a band which is only a trifle less strong than in the case of the esters. In the piperidide, however, the basic character of the substituent ($\cdot\text{NC}_5\text{H}_{10}$ instead of $\cdot\text{NH}_2$) is much more pronounced, and although the persistence of the band is increased from one to five exposures by the addition of alkali, there is no increase of absorptive power which would compare in any way with that observed in the case of the amide; the head of the band, indeed, is only extended by four exposures from 100 to 40 mm. of $N/100$ -solution, as contrasted with

* We have accepted here the ordinary representation of the enolic sodium salts

in preference to the alternative formula: $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{C} \begin{array}{c} \diagup \quad \diagdown \\ \text{ONa} \\ \text{OMe} \end{array} \\ \diagup \quad \diagdown \\ \text{CO} \end{array}$

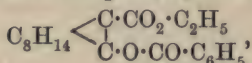
25 exposures from 100 to 0.25 mm. (actually to 25 mm. of $N/10,000$) in the case of the amide.

(4) The *acyl* derivatives. Three aliphatic acyl derivatives were examined, namely, the acetates of the methyl and amyl esters and the valerate of the ethyl ester. The curves for the three compounds are similar in form, showing a strong general absorption in the further part of the ultra-violet spectrum, but no absorption band. It is noteworthy that the curves run out very rapidly at the end of the spectrum, as if suggesting the possibility of a band at a frequency greater than that which can be reached with the iron arc and ordinary photographic plates. In accordance with the views advanced by Brühl, we accept for these compounds the enolic formula:



in spite of the wide difference which exists between their spectra and those of the corresponding sodium salts. This difference presents in a striking form the chief problem that arises from the experiments now described. The study of the derivatives of camphor-carboxylic acid alone would lead to the attachment of a fictitious importance to the metallic atom in the enolic salts; this error was corrected by the further study of the acyl derivatives, and a full discussion of the problem is therefore reserved for the following paper.

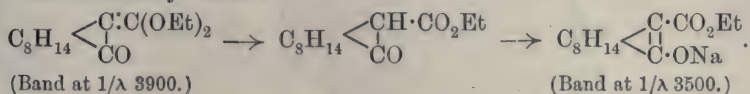
In addition to these three compounds, the crystalline benzoate,



of the ethyl ester was examined. In this case, also, the absorption curve was continuous, but instead of running out rapidly at the end of the spectrum, it was practically straight throughout. As its crystalline character afforded a unique guarantee of its purity (freedom from all traces of the parent ester), the absorption curve was also plotted in presence of sodium ethoxide. The development of a step-out or shallow band at $1/\lambda$ 3450 indicated, however, that the compound was already partly hydrolysed in the cold, and on boiling for a moment or two and again cooling, the deep band characteristic of alkaline solutions of the parent ester was produced.

The *diethyl* derivative of camphorcarboxylic acid requires separate consideration. The specimen lent to us by Prof. Brühl, an oil boiling at 164–165°/15 mm., gave a shallow band at $1/\lambda$ 3900, the head of the band being reached at a thickness of 20 mm. $N/1000$ -solution; on the addition of alkali the band was shifted to $1/\lambda$ 3500, and increased considerably in persistence, but appeared at much the same thickness as before. These results are in complete contrast

to the behaviour of the crystalline dimethyl derivative, which is fifty times less absorbent, shows a shallow band at $1/\lambda$ 3450, and is not affected at all by the addition of alkali. The band at $1/\lambda$ 3900 has no parallel amongst the derivatives of camphorcarboxylic acid, but appears to be closely related to those produced by the ethers of hydroxymethylenecamphor. Perhaps the most probable explanation of the observations is to suppose that the oil contains a certain proportion of an ester isomeric with the ordinary form, and that this is hydrolysed by alkalis, giving rise to the enolic sodium salts of the monoethyl ester:



(Band at $1/\lambda$ 3900.)

(Band at $1/\lambda$ 3500.)

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LXVI.—*Studies of Dynamic Isomerism. Part XI.*
The Relationship between Absorption Spectra and
Isomeric Change. Absorption Spectra of the Acyl
Derivatives of Camphor.

By THOMAS MARTIN LOWRY and HERBERT WILLIAM SOUTHGATE.

THE study of the acyl or carbonyl derivatives of camphor was undertaken in order to supplement the work on the carboxyl compounds which is described in the preceding paper. In carrying out the work we were indebted to Prof. Brühl for specimens of acetyl-, propionyl-, and butyryl-camphor and of the methyl and ethyl ethers of formyl- or hydroxymethylene-camphor; to Prof. Pope for specimens of the parent substance; its anhydride, acetate, and amino-derivative; to Dr. Glover for a specimen of methylenecamphor; and to Dr. Forster for a specimen of benzylidenecamphor and for specimens of α -benzoylcamphor and its derivatives. To all these we desire to express our thanks.

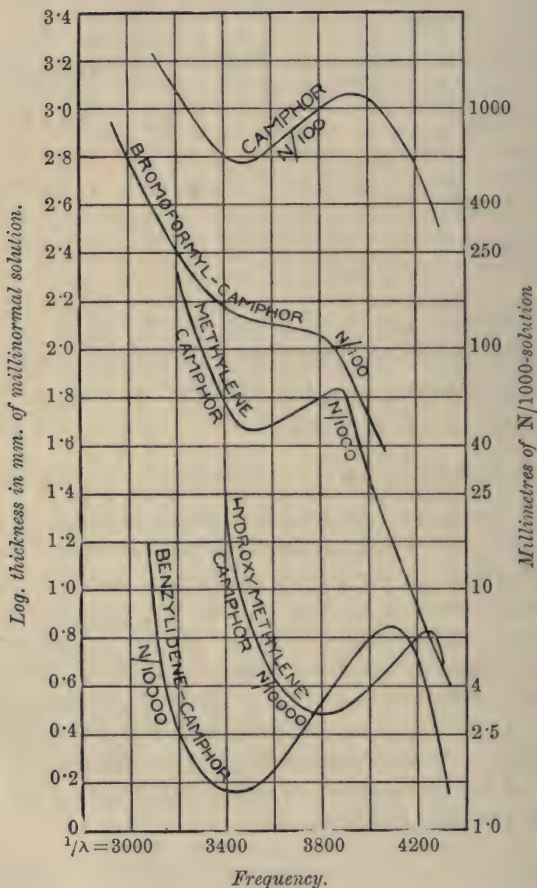
Unlike the carboxyl compounds, which show on the whole a very uniform behaviour, the acyl derivatives of camphor give rise to several types of absorption curve, even in the case of compounds which have usually been formulated in similar ways. This is notably the case amongst the derivatives of formyl- or hydroxymethylene-camphor, the curves being in some instances of such a character as to point unmistakably to the necessity of making an

alteration in the formulæ that have hitherto been generally accepted.

I.—*Hydroxymethylenecamphor and its Derivatives.*

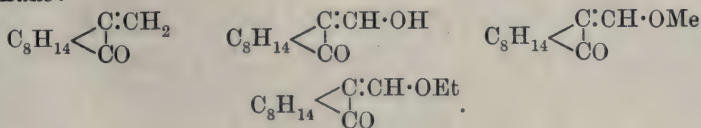
1. In contrast to methylenecamphor, which gives a shallow band, persisting over two exposures only, at $1/\lambda$ 3500, the spectrum of

FIG. 1.



the hydroxy-compound shows a strong band at $1/\lambda$ 3800 penetrating to a thickness of only 30 mm. of $N/10,000$ -solution. The same band is developed, with a slightly greater persistence, in the spectra of the methyl and ethyl ethers, which give two absolutely identical curves, the head of the band being reached at $1/\lambda$ 3775 and a

thickness of 20 mm. of $N/10,000$ -solution. There is no reason to doubt that these compounds are correctly represented by the formulæ:



Benzylidenecamphor, $\text{C}_8\text{H}_{14} \begin{array}{c} \diagup \text{C} \cdot \text{CHPh} \\ \diagdown \text{CO} \end{array}$, behaves in much the same way as the hydroxy-, methoxy-, and ethoxy-compounds, but gives a band of lower frequency.

2. On the addition of alkali, the curves for the methyl and ethyl ethers remain absolutely unchanged; but in the case of the parent substance there is a complete change of type,* the band at $1/\lambda$ 3800 being replaced by a still deeper band at $1/\lambda$ 3350. This band presents a striking resemblance to those which are produced by the enolic sodium salts of the camphorcarboxylic esters, and although the frequency at which it occurs is (for a reason that will be discussed later) slightly less than in the case of the carboxylic compounds, there can be no reasonable doubt that the change in the spectrum which results from the addition of alkali is again due to the formation of an enolic salt of the type shown in the formulæ:

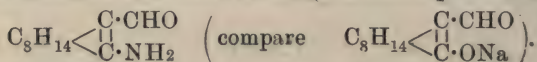


3. A change in the spectrum, precisely similar to that which results from the addition of alkali, also takes place when hydroxymethylenecamphor is converted by the action of ammonia into aminomethylenecamphor. The head of the band is again moved to $1/\lambda$ 3350, whilst its persistence extends over eleven exposures from 160 to 16 mm. of $N/10,000$ -solution. The two curves follow each other so closely† throughout their entire course that it is impossible

* The difference is much less pronounced in the curves than in the original photographs. On account of the rapid increase of dispersion in the far ultra-violet, the extension of the bands into this region gives a totally different appearance to the plate. The spectrum that is transmitted on the further side of the band is very weak and is liable to be obliterated by the general absorption of the solvent. The band at $1/\lambda$ 3800 in the spectrum of hydroxymethylenecamphor was indeed overlooked by Baly and Desch, who reported that the compound gave a continuous absorption curve; in the case of a band at $1/\lambda$ 4200 or beyond, the risk of a similar oversight is so great that ordinary methods would, in all probability, fail to disclose it, unless the conditions happened to be specially favourable.

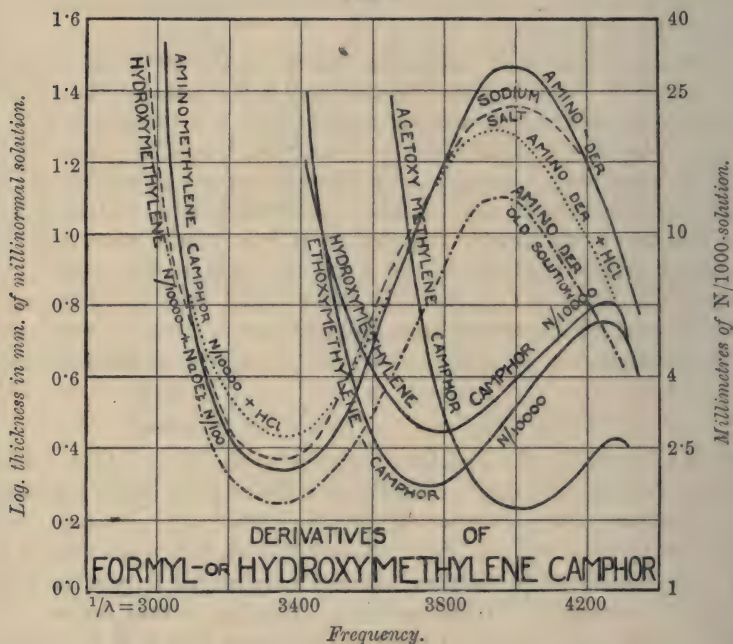
† The absolute identity of the curves for compounds containing the groups $\cdot\text{ONa}$ and $\cdot\text{NH}_2$ has already been noticed by Baly, and is of considerable value in deducing structural formulæ with the help of absorption curves. In comparing compounds containing the groups $\cdot\text{ONa}$, $\cdot\text{OH}$, and $\cdot\text{OAc}$, an allowance must be made for the

to resist the conclusion that the substances are similarly constituted, and that the correct formula for the amino-compound is:



The structure which we are thus led to assign to aminomethylene-camphor differs from that which has been adopted in all the earlier work on the substance (Bishop, Claisen, and Sinclair, *Annalen*, 1894, **281**, 331; Pope and Read, *Trans.*, 1909, **95**, 171), but gives

FIG. 2.



The broken line curve is for hydroxymethylenecamphor + NaOEt.

The dotted line curve is for aminomethylenecamphor + HCl.

The full curve on the left is for a fresh solution of aminomethylenecamphor; the dot-and-dash curve is for an old solution.

an equally good explanation of its physical and chemical properties, including the mutarotation phenomena discovered by Pope and

Read. The earlier formula, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C} \cdot \text{CH} \cdot \text{NH}_2 \\ \diagdown \text{CO} \end{array}$, may indeed represent

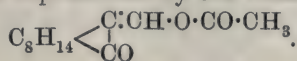
a minor constituent in the final equilibrium, but is quite untenable for the crystalline material to which the name and formula of displacement of the band which results from the interchange of these radicles even in compounds which are otherwise identical in structure.

aminomethylenecamphor have usually been assigned, the mere displacement of $\cdot\text{OH}$ by $\cdot\text{NH}_2$, which this formula postulates, being wholly inadequate to account for the transference of the band almost from end to end of the range of frequencies covered by the bands in the present series of compounds.

The addition of alkali produces in this case not the slightest alteration in the spectrum; the addition of acid reduced the persistence of the band by one exposure.

4. The anhydride of hydroxymethylenecamphor, like the sodium salt and the amino-derivative, shows a stronger selective absorption than the parent substance. The head of the band is at $1/\lambda$ 3500, and its persistence covers a range of nine exposures from 120 to 20 mm. of $N/10,000$ -solution (in this case 1 mol. in 20,000 litres). The absorption curve is at first absolutely unaltered by the addition of alkali, but after keeping for a day the original band is replaced by one at $1/\lambda$ 3350, owing (as the frequency shows) to the formation of the sodium salt by hydrolysis of the anhydride. The band produced by the anhydride falls in the middle part of the ultra-violet spectrum, and is entirely different from that produced by the parent substance and by its methyl and ethyl ethers; the latter are of special importance in this connexion, as there is no reason why the anhydride, which is itself an ether, should differ from other derivatives of this class unless its formation were accompanied by some change in the structure of the molecule. We are therefore unable to accept the formula, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{CH}\cdot\text{O}\cdot\text{CH}:\text{C} \\ \diagup \quad \diagdown \\ \text{CO} \quad \text{OC} \end{array} \text{C}_8\text{H}_{14}$, usually assigned to the compound, and prefer to regard it as an enolic compound, $\text{C}_8\text{H}_{14} \begin{array}{c} \text{C}:\text{CH}:\text{O} \quad \text{O}:\text{CH}:\text{C} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \\ \text{C} \quad \text{O} \quad \text{C} \end{array} \text{C}_8\text{H}_{14}$, of the same type as the sodium salt and the amino-derivative. From these compounds it differs only by 150 units in frequency, and even this difference can be accounted for as a normal result of displacing $\cdot\text{OH}$ or $\cdot\text{O}\cdot$ by $\cdot\text{ONa}$ or $\cdot\text{NH}_2$.

5. The crystalline acetyl derivative resembles the parent substance in giving a band in the far ultra-violet. The head of the band is at $1/\lambda$ 4025, and the persistence extends over two exposures from 25 to 20 mm. of $N/10,000$ -solution. As compared with hydroxymethylenecamphor and its ethers, the acetate gives a band of higher frequency and smaller persistence, but as this is the normal result of displacing $\cdot\text{OH}$ or $\cdot\text{OEt}$ by $\cdot\text{OAc}$, we believe that the two compounds are similarly constituted, and that the acetyl-derivative should be represented by the formula:



6. The bromo-compound, $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{CBr} \cdot \text{CHO} \\ | \\ \text{CO} \end{smallmatrix}$, the only direct derivative of formylcamphor in this series of substances, gives a continuous absorption curve with a rapid extension at $1/\lambda$ 3600. The curve resembles that for *aa'*-dibromocamphor.

II.—Acetyl-, Propionyl-, and Butyryl-camphor.

The absorption spectra of these compounds and their salts show a broad general resemblance to those of formyl- or hydroxymethylencamphor and its sodium derivative. The bands are as follows:

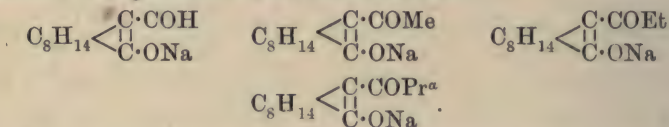
Parent Substances:

	Head of band. $1/\lambda$.		Persistence.
Formylcamphor ...	3800	4 exposures, from	64 to 30 mm. of <i>N</i> /10,000 solution
Acetylcamphor ...	3575	4 " "	90 to 40 " " "
Propionylcamphor..	3575	3 " "	90 to 50 " " "
Butyrylcamphor ...	3550	6 " "	30 to 10 " <i>N</i> /1000 "

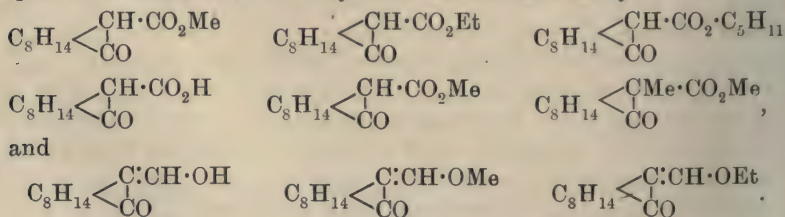
Sodium Derivatives (100 equivalents NaOEt):

Formylcamphor ...	3350	10 exposures, from	160 to 20 mm. of <i>N</i> /10,000 solution
Acetylcamphor ...	3300	10 " "	125 to 15 " " "
Propionylcamphor..	3250	10 " "	125 to 15 " " "
Butyrylcamphor ...	3200	11 " "	200 to 20 " " "

It will be seen that the sodium salts exhibit a fairly regular gradation, in agreement with the formulæ:



In the case of the parent substances, however, there is an abrupt break on passing from the formyl to the acetyl, propionyl, and butyryl compounds. This break is altogether exceptional, as there is nothing to correspond with it in the case of the sodium salts, nor in the three closely related homologous series, the absorption spectra of which have already been described, namely:



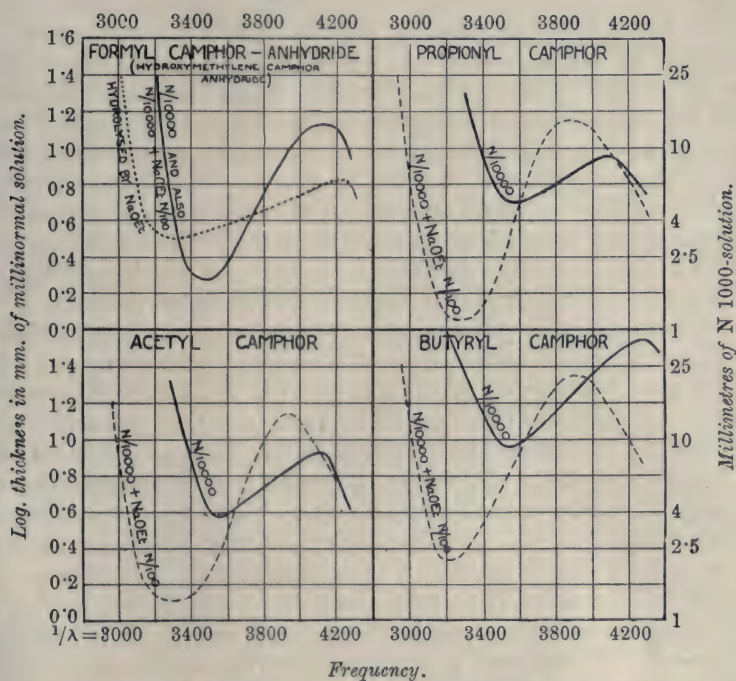
It can therefore scarcely be doubted that the transition from the formyl to the acetyl compound is accompanied by some change of

structure analogous to that which we have postulated as occurring in the conversion of hydroxymethylenecamphor into its amino-derivative.

In drawing this conclusion it must be borne in mind that the three higher homologues are liquid, and may well consist of mixtures of isomerides in equilibrium. Brühl (*Ber.*, 1904, **37**, 761), from an examination of their refractive and dispersive powers, concluded

FIG. 3.

Acyl derivatives of camphor.



Curves for alkaline solutions are drawn with broken lines.

that the four compounds were similar in structure, and might all be represented by the formula $C_8H_{14} \begin{smallmatrix} C:CR \cdot OH \\ | \\ CO \end{smallmatrix}$. This view we believe to be untenable in the light of the evidence now put forward. In our opinion the main constituent of the three liquid diketones is the "enol," $C_8H_{14} \begin{smallmatrix} C \cdot CO \cdot R \\ | \\ C \cdot OH \end{smallmatrix}$, from which the salts are derived, but the isomeric "enols" formulated by Brühl may also be present in large or small quantities. It may be pointed out that,

whilst the refractometric method would serve to distinguish the ketonic and enolic forms of these compounds, it would scarcely be likely to give distinctive values for the two enols, in view of the fact that each of these contains the same combination of an ethenoid linking with carbonyl on one side, and hydroxyl on the other.

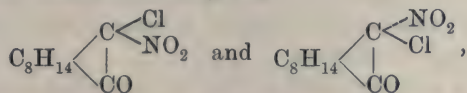
III.—*Origin of the Absorption Bands: Ketonic Compounds.*

In considering the origin of the absorption bands in this series of compounds, we are greatly helped by the fact that most of them contain only carbon, hydrogen, and oxygen, their absorptive properties being therefore evidently due either to the oxygen atoms or to ethenoid linkings between the carbons. Again—in marked contrast to the benzene series, where the simplest changes, including even the replacement of hydrogen by methyl, may produce a complete alteration in the spectrum and where the introduction of an absorbent group, instead of giving rise to an additional band, often obliterates those already present in the spectrum of the parent substance—the camphor compounds show a very simple and regular behaviour, and furnish admirable material for building up a theory of the origin of colour and of selective absorption in general.

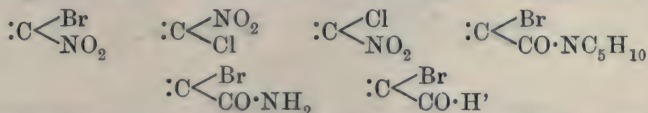
Monoketones.—In this connexion the presence of a shallow band in the spectrum of camphor itself is of great importance as indicating that the carbonyl group may give rise to a banded absorption even when linked to inert paraffinoid radicles; this property is not possessed by the hydroxylic oxygen of the alcohols, nor by the ethers and oxides in which the oxygen is linked to two different carbon atoms. It is also remarkable that even the carbonyl group is unable to produce an absorption band when directly linked to oxygen, as in the carboxylic acids and their derivatives. Both facts—the activity of the carbonyl and the inactivity of the carboxyl group—appear to have their origin in the residual affinity of the oxygen atoms. In the carbonyl group the absorbing system is probably not $>\text{C}:\text{O}$, but $>\text{C}:\text{O}^\cdot$, the double unsaturation giving rise to a much greater absorption than in the case of the alcohols and ethers, $>\text{O}^\cdot$, or of the olefines, $>\text{C}:\text{C}<$, in each of which only one such unsaturated or absorbent centre is present. In the carboxylic acids, on the other hand, there is probably (as Smedley and others have suggested) a cancelling of residual affinities, the group $\text{C} \cdot \begin{smallmatrix} \text{O}^\cdot \\ \diagup \\ \text{OH} \end{smallmatrix}$ becoming $\cdot\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{OH} \end{smallmatrix}$, or simply $\cdot\text{C} \begin{smallmatrix} \text{O} \\ \diagup \\ \text{OH} \end{smallmatrix}$. This view, which

affords an explanation of many of the observations recorded in the preceding pages, is amply supported by evidence derived from a study of the refractive properties of compounds containing these groups (Smedley, *Trans.*, 1909, **95**, 218, 231).

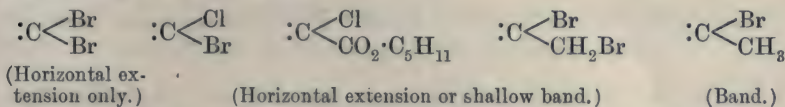
The variations of absorptive power produced by introducing different radicles into the camphor molecule (Lowry and Desch, Trans., 1909, **95**, 807, 1340) we regard as due in part to the residual affinity of the substituents, but the "distortion" of the ring-system (Armstrong and Robertson, Trans., 1905, **87**, 1276) is probably also a factor of importance. This latter factor may account, for instance, for the difference between the absorption curves of the stereoisomeric chloronitrocampfors:



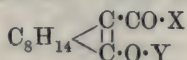
and for the strengthening of the band on passing from camphor to α -methylcamphor. On the other hand, the obliteration of the band in $\alpha\alpha'$ -dibromocamphor might be attributed either to the heavy but symmetrical loading of the α -carbon atom or to a general absorption, due to the residual affinities of the :CBr_2 group, pushing in from the further ultra-violet and covering up or obliterating the camphor band. The latter view is supported by the fact that the presence of two unsaturated radicles in the α -position invariably results in the reduction or removal of the band, as is seen in the following instances, in which the band disappears altogether:



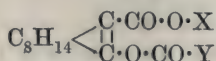
whilst a horizontal extension or shallow band is found when one of the two substituents ($-\text{Cl}$, $-\text{CH}_2\text{Br}$, $-\text{CH}_3$) is more or less fully saturated, as in the series:



The general absorption, which is the chief feature of the curves for all but the last of the above compounds, is probably due to some play of residual affinities of the same general character, but of less intensity than that which gives rise to a band. An actual case in which a band is converted into a general absorption by the locking up of residual affinities which takes place when

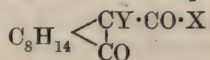


becomes



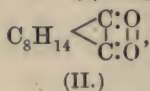
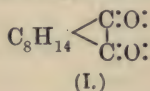
is discussed below.

α- and β-Diketones.—The β-diketones represented by the formula



possess absorptive properties of the same order as those of the parent monoketone. So far as their absorptive power is concerned, there is, therefore, no evidence of any co-operative action between the two ketonic groups. This is also true, as Brühl has shown (*Ber.*, 1902, **35**, 3515), of the molecular refractive and dispersive powers, and our own observations of magnetic rotatory dispersion have led to similar conclusions.

In the case of camphorquinone, on the other hand, although the refractive power is substantially normal (W. H. Perkin, sen.; Armstrong and Robertson, *Trans.*, 1905, **87**, 1275, 1292), the contiguity of the two carbonyl groups leads to a remarkable development of absorptive power; the band at $1/\lambda$ 2050 falls within the visible region and gives rise to visible colour, whilst its persistence extends from 250 to 4 mm. of *N*/10-solution, a range corresponding with no less than 16 of our logarithmic exposures* (Stewart and Baly, *Trans.*, 1906, **89**, 496). The system which produces these exceptional effects is probably represented only incompletely by the conventional formula, and should be shown as (I) or possibly as (II):



the latter formula resembling the symbol :O:O: suggested by Armstrong for gaseous oxygen, but with the bonds all bound instead of partly free.

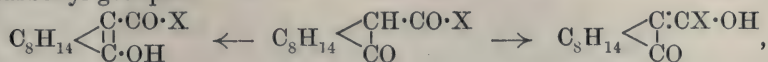
IV.—*Origin of the Absorption Bands: Enolic Compounds. Factors which influence the Persistence of the Bands.*

Whilst the carbonyl derivatives of camphor are, as β-diketones, incapable in their ordinary form of developing any co-operative action between the two ·CO· groups, copulation in the usual sense, as expressed by the symbol :C·C:, is of frequent occurrence amongst their enolic isomerides, and it is to this fact that the intensity of so many of the bands may most readily be attributed.

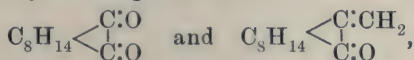
Enolisation may occur in two ways, giving rise to derivatives

* It is noteworthy that the "penetration" of the band (to which we attach considerable importance) is not appreciably greater in camphorquinone than in camphor; the band is, therefore, of less value than a casual reference to its persistence or to the appearance of the absorption curves might indicate, and is, indeed, remarkable mainly for the low frequency which brings it within the visible region of the spectrum and away from the region of strong general absorption rather than for any exceptional intensity in the local absorption.

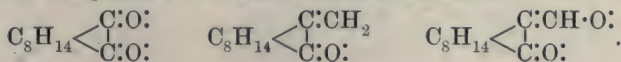
either of hydroxycamphene or of methylenecamphor, according as the mobile hydrogen atom is transferred to one or other of the two carbonyl groups:



Each of these forms contains the group $\cdot\text{C}:\text{C}:\text{C}:\text{O}\cdot$, and may give rise to banded absorption owing to the copulation of the ethenoid linking with the carbonyl group; the effects produced are, however, much less striking than when two carbonyl groups are copulated. Thus, in spite of the superficial resemblance between camphorquinone and methylenecamphor,



the absorptive properties of the two compounds are entirely different, methylenecamphor (when pure) possessing no visible colour, and even in the ultra-violet region giving rise only to a shallow band persisting over no more than two exposures. This difference is no doubt due to the lack of residual affinity in the methylene group. The deficiency in this respect can, however, be made good by the introduction of a hydroxyl group into the methylene, when a well-marked band appears at the further end of the ultra-violet spectrum. The bonds and residual affinities of the three compounds are shown in the formulæ:



The utilisation of an alcoholic oxygen atom as a direct agent for the development of colour is a possibility that is not very widely recognised, but there can be no doubt as to the importance of the part which it plays in the production of a band in this series of compounds.

The efficiency of the oxygen atom as a third centre of absorption is not affected by etherification, as may be seen by referring to the spectra of the ethers of hydroxymethylenecamphor. Esterification, on the other hand, produces a marked reduction of persistence, the band of acetoxymethylenecamphor extending over two exposures only as compared with four exposures in the parent substance and five in the ethers. This effect is very similar to that produced by converting a carbonyl into a carboxyl group, and may again be attributed to the cancelling or locking-up of residual affinities. The two groups, $\cdot\text{O} \cdot \text{CO} \cdot \text{CH}_3$ and $\cdot\text{CO} \cdot \text{O} \cdot \text{CH}_3$, are indeed almost equally valueless so far as the production of absorption bands is concerned.

A contrary effect is produced when the hydroxyl group is displaced by $\cdot\text{ONa}$ or by $\cdot\text{NH}_2$, the power to develop a band being

much greater in the salts and in the amino-compounds than in the alcohols from which they are derived. This effect may also be attributed to the influence of residual affinity, since the quinquevalency of nitrogen is far more pronounced, and has been recognised for a longer period than the quadrivalency of oxygen, whilst a comparison of sodium hydroxide with water is sufficient to indicate that the introduction of the metal may result in a marked increase in the affinity of the molecule.

One other factor which influences the efficiency of the absorbing system may be noticed, namely, the bridging of the ethenoid linking by a chain of carbon atoms. The increased absorptive power which this produces is clearly seen on comparing the absorption band of hydroxymethylenecamphor, $C_8H_{14} \begin{smallmatrix} \diagup & C \cdot CH \cdot OH \\ | & | \\ & C : O \end{smallmatrix}$, with that of the anhydride, in which this group becomes $C_8H_{14} \begin{smallmatrix} \diagup & C \cdot CH : O \\ | & | \\ & C : O \end{smallmatrix}$. The transference of the ring-system from the single to the double bond is here accompanied by an increase in the persistence from four to nine exposures.

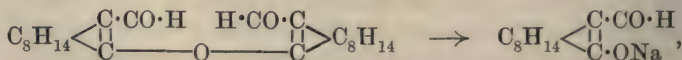
General and Specific Absorption: Persistence or Penetration as a Measure of the Intensity of a Band.

The question of the intensity or persistence of a band is closely related to that of the frequency at which it occurs. In general an increase in the efficiency of the absorbing centres is required, not only to increase the persistence of a band, but also to reduce the frequency at which it occurs. It is for this reason that visible colour so rarely occurs, the whole of the compounds now under discussion being colourless, with the single exception of camphorquinone; it is for this reason, also, that, as Armstrong has pointed out, the co-operation of three absorbing centres is so frequently needed to produce this effect.

In the present series of compounds it has been found that an increase of persistence and a decrease of frequency occur together when an alcohol or its ether is converted into a salt, for example:



or



whilst a decrease of persistence and an increase of frequency accompany the conversion of the alcohol into its ester, for example:



or



On the other hand, in the transition from the sodium salt to the amino-derivative of hydroxymethylenecamphor, the persistence and the frequency are alike unchanged. Analogous observations of each of the above types have been recorded by Baly in the benzene series, and the effects produced are probably general in their application.

For this association of high frequency with small persistence in a series of bands of equal "penetration," an a priori reason may perhaps be found in the general absorption, spreading inwards from the far ultra-violet, which all substances show in a greater or less degree. If a typical curve of general absorption be drawn from $1/\lambda$ 4400 at 1 mm. thickness to $1/\lambda$ 3200 at 100 mm. thickness, and an absorption band penetrating to a thickness of 1 mm. be superposed on it, it will be found that the band is cut off by the general absorption at a smaller and smaller thickness as the frequency is increased. In a typical case the following values were found:

Frequency	3000	3200	3400	3600	3800	4000	4200	4400
Log. persistence ...	1.5	1.1	0.8	0.6	0.4	0.2	0.1	0.0

From this table it is clear that a local absorption of constant intensity will produce a band of less and less persistence as the frequency increases, and that finally a point may be reached at which the band disappears altogether beneath the general absorptive power of the compound. In a case of this sort the penetration rather than the persistence appears to be the true measure of the intensity of the band.

Precisely such conditions appear to prevail amongst the enolic compounds now under discussion, as is seen, for instance, amongst the derivatives of hydroxymethylenecamphor:

Substance.	Amino- derivative.	Sodium salt.	Anhydride.	Ethers.	Alcohol.	Acetate.
Frequency	3350	3350	3475	3775	3800	4025
Log. penetration *	0.2	0.2	0.3	0.3	0.5	0.3
Log. persistence ...	1.1	1.0	0.9	0.5	0.4	0.2
„ (calculated)	0.9	0.9	0.7	0.4	0.4	0.2

* The "penetration" of the band is expressed here by the logarithm of the thickness in mm. of millinormal solution used for the last exposure in which the band appears. Under constant experimental conditions, the values are fairly concordant, but large changes are produced if the intensity of the light or the time of exposure and depth of development of the plate are altered. The slight cloudiness or opalescence which usually results from the addition of alkali to the alcoholic solutions appears to reduce the penetration by about 0.2, but this effect is not produced if the alcohol has been distilled from potassium hydroxide. The persistence is expressed by the logarithm of the ratio of the first and last thicknesses at which the band is seen.

The penetration of the band * is substantially uniform throughout, but the persistence steadily decreases as the frequency increases. A comparison of these values with the fictitious absorption curves described above shows a very close general agreement, as is shown in the last line of the table. The agreement is, indeed, as close as can be expected, in view of the fact that the hypothetical curve of general absorption was merely sketched in (the band was copied from an actual curve), and the only adjustment made was to shift it through 200 units in the direction of greater frequency so as to give a better comparison.

The uniformity of penetration which characterises the bands produced by hydroxymethylenecamphor and its derivatives extends to all the enolic compounds described in this and in the preceding paper. Thus, in the case of camphorcarboxylic acid, the enolic sodium salt of the amide gives a band of penetration 0.4, whilst for the esters the values are 0.2, 0.0, 0.3. For the sodium derivatives of the acyl-camphors, the values are 0.2, 0.1, and 0.4, the parent substances, which are probably mixtures of isomerides in equilibrium, giving higher values, 0.6, 0.7, and 1.0. The derivatives of α -benzoylcamphor give values ranging from 0.2 to 0.5, whilst benzylidenecamphor gives the value 0.2. From these observations it may be concluded that the three copulated centres of absorption which are present in all these compounds give rise to a local absorption of uniform intensity, but that the introduction of various groups alters the frequency at which the maximum of absorption occurs, the wide range of persistences being due far more to these alterations of frequency than to any change in the intensity of the local absorption. These considerations may even be applied to the acyl derivatives of the camphorcarboxylic esters which give no band at all, owing, in all probability, to the fact that an increase of frequency to, say, $1/\lambda$ 4400 submerges the band beneath the general absorption of the compound.

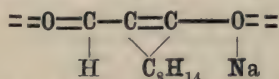
The uniformity of penetration which characterises the bands of the enolic compounds extends also to the ketonic compounds, although the reduction in the number of copulated centres of absorption from 3 to 1 causes the band to cease at a much greater thickness (antilog 3.0 instead of 0.3). This is seen clearly in the case of camphorcarboxylic acid and its derivatives, for example:

Acid	2.9	Methyl ester	3.1
Sodium salt	2.8	Ethyl ester	3.0
Amide	2.9	Amyl ester	3.1
Piperidide	3.0	Dimethyl ester	3.1

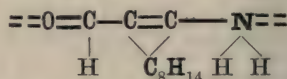
and also in the case of camphor itself (Lowry and Desch, *loc. cit.*), where, with a shorter period of exposure, the values were for

* See footnote, p. 917.

The introduction of a sodium atom or the displacement of $\cdot\text{OH}$ by $\cdot\text{NH}_2$ causes a further development of residual affinity, and the band advances again through 150 units to $1/\lambda$ 3350:

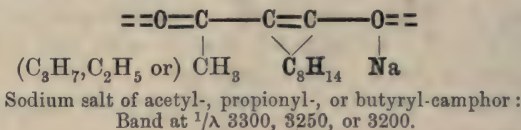


Sodium salt: Band at $1/\lambda$ 3350.



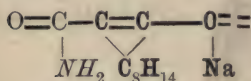
Amino-derivative: Band at $1/\lambda$ 3350.

The sodium salts of the acyl derivatives of camphor give almost identical bands at $1/\lambda$ 3300 to 3200:

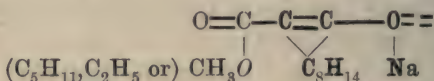


In these compounds the band reaches its maximum development in the series of substances now under consideration: the phenyl group in the sodium salt of α -benzoylcamphor causes a further transference of the band in the direction of the visible region, but the discussion of the observations made with this substance is withheld until further information is available as to the influence of the phenyl group on the spectra of various types of compounds.

The sodium salts derived from the amide and esters of camphor-carboxylic acid illustrate the reduction of residual affinity which results from the conversion of a carbonyl into a carboxyl group. The band retreats through 100 units to $1/\lambda$ 3450, but the presence of the sodium atom prevents any serious decay of absorptive power:



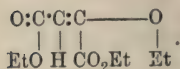
Sodium salt of amide:
Band at $1/\lambda$ 3450.



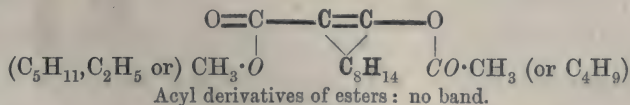
Sodium salt of esters:
Band at $1/\lambda$ 3450.

Unfortunately, no corresponding enolic derivatives are known* which contain the group $\cdot\text{OH}$ or $\cdot\text{OEt}$, and it is necessary to pass direct from the positive influence of the $\cdot\text{ONa}$ group to the negative influence of the $\cdot\text{OAc}$ group. When the absorbent system is thus weakened at each extremity, its powers of resistance fail, and the

* Baly and Desch (Trans., 1904, **85**, 1035; 1905, **87**, 778) found no band in the spectra of ethyl ethoxycrotonate, $\begin{array}{c} \text{O:C:C:C—O} \\ | \quad | \quad | \quad | \\ \text{EtO} \quad \text{H} \quad \text{Me} \quad \text{Et} \end{array}$, and ethyl ethoxyfumarate,



band disappears altogether in the acyl derivatives of the above esters:



in spite of the fact that the bridging of the ethenoid linking continues to give to the central group of the system its maximum efficiency. In these compounds the minimum of selective absorption is reached, the ethenoid linking supported only by the two weak groups shown in the formula $\text{C}_8\text{H}_{14} \begin{smallmatrix} \text{C} \cdot \text{CO} \cdot \text{O} \cdot \text{Me} \\ | \\ \text{C} \cdot \text{O} \cdot \text{CO} \cdot \text{Me} \end{smallmatrix}$ being incapable of developing any specific absorptive power of low enough frequency or deep enough penetration to emerge from the general absorption of the compound within the limits in which it could be observed by the usual experimental methods.

In setting out the views described above, no claim is made for absolute originality; the object in view was the purely practical one of arriving at a satisfactory explanation of a somewhat complicated series of absorption curves. In doing this the fullest use has been made of Armstrong's theories as to the origin of visible colour, and his conceptions of residual affinity; the most casual perusal of the paper will show the large extent to which we are indebted to the ideas which he has advocated so persistently during a long period of years. We have also been influenced largely by Baly's work on absorption spectra and by the contemporary publications of Flürscheim and others on the distribution and transmission of residual affinity in the molecule.

The materials used in the researches now described were for the most part lent to us by other workers, to whom we have already expressed our thanks; the incidental expenses have been defrayed in part by a grant from the Research Fund of the Chemical Society, and we desire to place on record our indebtedness for the help thus received.

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WESTMINSTER, S.W.

LXVII.—*Studies in Fermentation. Part III. The Rôle of Diffusion in Fermentation by Yeast Cells.*

By ARTHUR SLATOR and HENRY JULIUS SALOMON SAND.

WHEN a fermentable sugar is transformed into alcohol and carbon dioxide by the action of living yeast suspended in an aqueous solution of the sugar, it is generally accepted that the chemical action takes place within the yeast cell, and that the sugar has to diffuse into the latter before it is attacked by the enzyme. A consideration of the influence of various factors on the rate of alcoholic fermentation shows that under ordinary conditions diffusion supplies the yeast cells rapidly and efficiently with sugar. The high temperature-coefficient and the constancy of the velocity with different concentrations of the sugar constitute practically conclusive evidence on this point. It is, however, conceivable that under certain conditions, such as with very dilute sugar solutions, or with very active yeast cells, diffusion could not take place rapidly enough to supply the yeast cells with sugar to enable them to exert their maximum fermentative power. In the present investigation the limiting conditions have been examined under which diffusion alone would no longer be capable of supplying the yeast cells efficiently with sugar, and under which the apparent velocity of the reaction would thus be influenced by convection currents produced either owing to the evolution of gas in the liquid, or by external means.

In order to obtain an insight into the extent to which such convection currents (stirring) might conceivably affect the rate of fermentation by yeast cells, it is useful first to determine what are the maximum differences of concentration which might arise in a liquid in which no convection currents whatever take place, and in which uniformly distributed yeast cells are operative.

It will be readily conceded that if we place a single yeast cell in the centre of a spherical vessel containing a sugar solution, differences of concentration between the surface of the cell and the boundary of the vessel will arise, which will at first increase and become the greater the further away the boundary of the vessel is. These differences of concentration will attain their greatest value if no diminution of the concentration in the outermost layer is allowed to take place and if the yeast cell has been operative for an indefinite period of time, so that the "permanent" state has been attained. In the latter case the amount of sugar removed by the yeast cell per unit of time is the same as that flowing to it, owing to diffusion across any concentric spherical surface inside the sphere.

The amount of sugar F removed by each yeast cell per unit of time can be determined from experiments, the cell may be assumed to be of spherical shape, and a sufficiently accurate value assigned to its radius. It might at first sight be assumed from analogy to diffusion in a straight line (unidimensional) that a permanent state could only be attained after the concentration on the surface of the yeast cell had diminished to zero. That this is by no means the case has already been proved in the paper by one of us (Sand, *Proc. Roy. Soc.*, 1905, **74**, 356), in which a similar problem was treated. This problem was, however, rather different from that at present under discussion, and it will be convenient to deduce directly the formulæ required to suit the present case.

The first part of our problem thus consists in determining what is the concentration at the surface of a spherical yeast cell of radius R placed at the centre of a spherical vessel of infinite radius on the boundary of which the concentration C is maintained. The yeast cell removes a quantity of sugar F by chemical action per unit of time. Imagine the spherical vessel subdivided by a large number of concentric, spherical surfaces of radius x and surface $4\pi x^2$. Across each of these the amount of sugar F diffuses per unit of time. Indicating the diffusion-coefficient of the sugar by κ and the concentrations by C , we have:

$$F = 4\pi\kappa x^2 \frac{dc}{dx} \quad . \quad . \quad . \quad . \quad (1),$$

with the limiting condition:

$$c = C \text{ for } x = \infty \quad . \quad . \quad . \quad . \quad (1a).$$

The integral of the above equation under the condition 1a is:

$$C - c = \frac{F}{4\pi\kappa x} \quad . \quad . \quad . \quad . \quad (2),$$

and indicating the concentration of the sugar on the outside of the yeast cell by C_1 and the radius of the latter by R , we have:

$$C - C_1 = \frac{F}{4\pi\kappa R} \quad . \quad . \quad . \quad . \quad (2a).$$

The equation 2a thus allows us to calculate the maximum conceivable difference of concentration that might arise between the surface of the yeast cell and other parts of the liquid if no stirring whatever takes place.

We now come to the consideration of the changes of concentration of the sugar solution which arise in the interior of the yeast cell owing to the combined influences of chemical action and diffusion. We may assume the enzyme to be uniformly distributed throughout the yeast cell, and we know the velocity of the reaction to be

independent of the concentration of the sugar within wide limits, so that this velocity may be assumed to be uniform throughout the whole cell (see Trans., 1906, **89**, 133). Indicating therefore by s the amount of sugar removed in the interior of the cell by chemical action per unit of volume and time, and employing the same notation as above, we have:

$$s = \frac{F}{\frac{4}{3}\pi R^3} \quad . \quad . \quad . \quad . \quad . \quad (3).$$

We proceed to calculate the concentration of the sugar c corresponding with any point in the yeast cell at a distance r from its centre after the permanent state has been attained. The latter, as can be seen from other considerations, is approached with exceedingly great rapidity (compare Sand, *loc. cit.*). We imagine the yeast cell divided into an infinite number of concentric, spherical shells of radius r , thickness dr , and thus of volume $4\pi r^2 dr$. If we indicate the amount of sugar flowing (owing to diffusion) into a shell towards its centre per unit of time at the radius $r + dr$ by $f_{(r+dr)}$, and the amount flowing out at a radius r by $f_{(r)}$, and, further, the amount removed in the shell by chemical action by S , then, when the permanent state is established, we have:

$$S + f_{(r)} = f_{(r+dr)}$$

or

$$S = df \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Further, we have:

$$S = 4\pi r^2 s dr \quad . \quad . \quad . \quad . \quad . \quad (5).$$

$$f = 4\pi \kappa r^2 \frac{dc}{dr} \quad . \quad . \quad . \quad . \quad . \quad (6).$$

(f , c , and r are variables)

Differentiating (6) and substituting the result and the value of S from equation (5) into equation (4), we find:

$$4\pi r^2 s dr = \left(8\pi \kappa r \frac{dc}{dr} + 4\pi \kappa r^2 \frac{d^2c}{dr^2} \right) dr$$

or

$$\frac{s}{\kappa} = \frac{2}{r} \frac{dc}{dr} + \frac{d^2c}{dr^2} \quad . \quad . \quad . \quad . \quad . \quad (7),$$

the limiting conditions being $f = F$ for $r = R$, and $c = C_1$ for $r = R$.

The integral of equation (7) is:

$$c = \frac{\text{const.}_1}{r} + \frac{1}{6} \frac{s}{\kappa} r^2 + \text{const.}_2,$$

and the limiting conditions yield the values:

$$\text{const.}_1 = 0; \quad \text{const.}_2 = C_1 + \frac{1}{6} \frac{s}{\kappa} R^2,$$

which, in conjunction with (3), lead to:

$$C_1 - c = \frac{s}{6\kappa} (R^2 - r^2) = \frac{F}{8\pi\kappa} \frac{R^2 - r^2}{R^3}.$$

From this equation we find for the concentration C_0 at the centre of the cell ($r=0$):

$$C_1 - C_0 = \frac{F}{8\pi\kappa R} \quad . \quad . \quad . \quad . \quad . \quad (8).$$

This result represents the maximum difference of concentration to be found in the yeast cell; and, with maximum stirring of the liquid (during which C_1 is the average concentration of the liquid), it also represents the maximum difference of concentration arising throughout the system. With minimum stirring of the liquid, we find by combination with equation 2a for the greatest difference in concentration to be met with in the system:

$$C - C_0 = \frac{3}{8} \frac{F}{\pi\kappa R} \quad . \quad . \quad . \quad . \quad . \quad (9).$$

that is, a value three times as great as the foregoing.

The value of F for brewery yeast was determined experimentally by means of the apparatus described in previous publications (Trans., 1906, **89**, 128; *J. Soc. Chem. Ind.*, 1908, **27**, 653). A solution of dextrose and a known quantity of yeast cells, the number of which was determined by means of a hæmacytometer, were introduced into the bottle of the apparatus and the velocity of fermentation measured on the manometer scale. An absolute value of the velocity was obtained after calibration of the apparatus, the latter operation being carried out by fermenting a known weight of dextrose and observing the corresponding change in pressure. From these measurements can be calculated the number of grams of dextrose fermented per second by a yeast cell of average activity. The results of four experiments with different samples of yeast are given in the following table:

Temperature, 30°. Volume of liquid = 60 c.c.

Concentration of dextrose = 5 grams per 100 c.c.

,, ,, yeast = 1 gram of pressed yeast per 100 c.c. (approximately).

Number of yeast cells in 60 c.c.	Grams of dextrose fermented per second.	F .
2.10×10^9	6.2×10^{-5}	3.0×10^{-14}
1.91×10^9	6.2×10^{-5}	3.2×10^{-14}
1.79×10^9	5.0×10^{-5}	2.8×10^{-14}
2.07×10^9	6.0×10^{-5}	3.0×10^{-14}

At this concentration of the uniformly distributed yeast, the average concentration of the sugar decreases so slowly that the

permanent state for which our formulæ have been deduced is, for practical purposes, reached so quickly, that during its attainment there is no appreciable variation of the outside concentration C . We may also express this by saying that the yeast cells do not appreciably interfere with each other's action.

For purposes of calculation, the value $F = 3 \times 10^{-14}$ gm./sec. has been taken. The diameter of the yeast cells is approximately 8μ , giving $R = 4 \times 10^{-4}$ cm. The diffusion-coefficient of dextrose, κ , is approximately 7×10^{-6} cm.²/sec.*

Substituting the values in equations 8 and 9, we have:

$$C_1 - C_0 = \frac{3 \times 10^{-14}}{8 \times \pi \times 7 \times 10^{-6} \times 4 \times 10^{-4}} = 4.3 \times 10^{-7} \text{ gm./cm.}^3.$$

$$= 0.43 \text{ mg. per litre.}$$

and

$$C - C_0 = 1.29 \quad , \quad , \quad ,$$

The maximum difference of concentration brought about in the system with stationary uniformly distributed cells is therefore about 1.3 milligrams per litre. Two-thirds of this difference can be removed by stirring. If we make $C_0 = 0$, we obtain conditions under which there diffuses into the yeast cell just enough sugar as can be fermented by the cell. Diffusion therefore supplies the yeast cell efficiently with sugar unless the concentration falls below 1.3 milligrams per litre, or, with maximum stirring of the solution, a concentration a third as great will satisfy the condition. From equation 8 and 9 we can also calculate the activity of a yeast cell which could just entirely ferment the whole of the sugar diffusing into the cell. If the concentration of the sugar solution is 5 grams per 100 c.c. with maximum stirring of the solution, $C_1 = 5 \times 10^{-2}$ gram/cm.², and with minimum stirring, $C = 5 \times 10^{-2}$ gram/cm.². Further, making $C_0 = 0$, and denoting the number of grams of sugar fermented per second by F^1 , we have, with maximum stirring, $F^1 = 8\pi \times 7 \times 10^{-6} \times 4 \times 10^{-4} \times 5 \times 10^{-2} = 3.5 \times 10^{-9}$ gram/sec., and with minimum stirring, $F^1 = 1.2 \times 10^{-9}$ gram/sec. Yeast which would fulfil this condition in the first case would have to be 120,000 times as reactive as brewery yeast, and in the second case 40,000 times as reactive as brewery yeast.

It is also evident that the greater the yeast cell the more slowly is it supplied by diffusion with sugar. From equations 8 and 9 we can calculate the size of a yeast cell which would just entirely ferment the whole of the sugar diffusing into the cell, assuming

* So far as we are aware, the diffusion-coefficient of dextrose has not been determined, but as substances of about the same molecular weight have almost the same diffusion-coefficient, the value for dextrose cannot be greatly different from that of mannitol, which at 30° is $4.4[1 + (30^\circ - 10^\circ)0.025] \times 10^{-6} = 6.6 \times 10^{-6}$. It is assumed that the sugar diffuses in the yeast cell at the same rate as in water.

that this large cell is built up of material of the same activity as brewery yeast, that is, keeping F/R^3 constant:

$$\frac{F}{R^3} = \frac{3 \times 10^{-14}}{(4 \times 10^{-4})^3} = 4.7 \times 10^{-4}.$$

Substituting in equation 8, $C_1 = 5 \times 10^{-2}$, $C_0 = 0$,

and $F = R^3 \times 4.7 \times 10^{-4}$,

we obtain $R^2 = 1.87 \times 10^{-2}$ or $R = 0.14$ cm.

With maximum stirring of the solution, yeast cells of radius 1.4 mm. would therefore just be efficiently supplied by diffusion with dextrose from a solution containing 5 grams per 100 c.c. With minimum stirring, a value of the radius 0.8 mm. would satisfy the condition.

From these calculations we may conclude that during fermentation diffusion supplies the yeast cells very efficiently with sugar, and, further, it is unlikely that conditions could be experimentally realised under which diffusion becomes a controlling factor of the rate of fermentation.

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LXVIII.—*The Molecular Refraction of Thiocyanates and other Salts.*

By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

IN previous communications (Trans., 1906, **89**, 556; 1908, **93**, 684, 2148) it has been shown that the refraction value of the group $\cdot\text{NCS}$ is materially higher than that of the isomeric $\cdot\text{SCN}$ when these are conjoined with organic radicles. As calculated from the formula:

$$M_D = \frac{(\mu_D - 1)p}{dt^\circ/4^\circ}$$

(where M_D = molecular refraction, μ_D = index of refraction for the spectral line D , p = molecular weight, and $dt^\circ/4^\circ$ = density at t° , referred to water at 4°), the mean values for $\cdot\text{NCS}$ and $\cdot\text{SCN}$ were about 28.1 and 23.3 units respectively, the difference of 4.8 units depending no doubt in some way on the various linkings within the rhodanic group.

The mean refraction value of the whole complex, $\cdot\text{NCS}$, being calculated from the results of a considerable number of different measurements, is probably correct to within a few tenths of one unit on the above scale; the figures for $\cdot\text{SCN}$, however, although

fairly concordant with one another, were deduced from observations with only three different compounds, and hence it seemed desirable, as a preliminary towards determining the specific effects of the atomic linkings, to check by a larger number of observations the mean total value of the $\cdot\text{SCN}$ group.

As material for the purpose, we selected the metallic thiocyanates; for these substances, although differing somewhat in chemical properties from their organic congeners, are nevertheless related to them by constitution, in much the same way as metallic salts to the corresponding esters. Unlike the purely organic combinations, they are dissociated more or less readily by dissolution in water; but as the refraction values of salts in general vary to no considerable extent at different concentrations, and show in this respect no distinct regularity, it seems probable that the observed variations are due rather to slight errors of experiment than to the effect of electrolytic dissociation.

It is by no means easy to determine accurately the molecular refraction of a dissolved salt, even at moderate dilutions: thus, in a 5 per cent. solution of sodium chloride, each molecule of salt is associated with more than 60 molecules of water, the total effect, minus that due to the water, being taken as the refraction value of the dissolved salt. Supposing, as is approximately true, that each salt molecule exerts two and a-half times the effect of a water molecule, then, out of every 25 units of molecular refraction observed, more than 24 are due to the water molecules, and less than 1 to those of the salt; in such circumstances, the difficulty of securing measurements of high precision is obvious.

In determining the molecular refractive powers of the "metallic" thiocyanates in aqueous solution, we employed sodium light, the calculations being made by the formula:

$$\frac{(\mu - 1)100}{d} = \frac{(\mu' - 1)(100 - x)}{d'} + \frac{(\mu'' - 1)x}{d''},$$

where μ , μ' , and μ'' are the indices of refraction for the solution, the solvent, and the solute respectively; d , d' , and d'' the corresponding densities at $t^\circ/4^\circ$; and x the weight of salt in 100 parts, by weight, of the solution. From the specific refraction, $\frac{\mu'' - 1}{d''}$, thus calculated, the molecular refraction was determined by multiplying by the molecular weight, p :

$$M_D = \frac{(\mu'' - 1)p}{d''}.$$

Owing to the hygroscopic nature of the salts examined, it was found expedient to determine analytically the amount contained

in a weighed quantity of the solution, and for this purpose Volhard's method was employed.

The following table shows the results of the measurements. For the solvent (water) the indices of refraction and the densities are not given, the figures being accessible from tables of physical constants; the numbers in the right-hand column are obtained by deducting in each case from the molecular refraction, M_D , the mean atomic refraction of the basic constituent, taken as follows:

$$\text{Na}=4.4; \text{NH}_4=11.4; \text{Ca}=10; \text{Al}=7.7;$$

the residues, divided by the number of thiocyanogen groups per molecule, represent the refraction effect of one $\cdot\text{SCN}$ group. These "mean atomic refractions" are derived from measurements in which light corresponding with the C line was used, and hence are not quite accurate for the D line; the deviations, however, being probably one or two tenths of a unit, and hence no larger than the experimental errors, we have not considered it necessary to recalculate or to redetermine the values.

Refraction Value of $\cdot\text{SCN}$ in Certain Thiocyanates (line D).

	Salt.	Mols. H_2O to 1 mol. salt.	t° .	$dt/4^\circ$.	μ_D of solution.	M_D .	Value of $\cdot\text{SCN}$.
1	NH_4SCN	12.32	16°	1.0585	1.39634	37.49	26.09
2	NH_4SCN	4.71	15	1.1114	1.45521	37.55	26.15
3	NH_4SCN	6.28	15	1.0944	1.43617	37.63	26.23
4	NaSCN	11.27	18	1.1600	1.40250	30.35	25.95
5	NaSCN	6.66	18	1.2306	1.43336	30.81	26.41
6	NaSCN	5.66	18	1.2599	1.44461	30.54	26.11
7	$\text{Ca}(\text{SCN})_2$	17.55	17	1.2185	1.43356	62.51	26.26
8	$\text{Al}(\text{SCN})_3$	36.79	18	1.1582	1.41207	86.30	26.20

Salts 1 to 5 were purified by recrystallisation from 90 per cent. alcohol; Nos. 6 to 8 were used as purchased from Kahlbaum, the last being in aqueous solution. To the above figures may be added Gladstone's result for potassium thiocyanate, namely, 33.95* (*Journ. Chem. Soc.*, 1870, **23**, 107); this, less 7.9 for K, leaves $\cdot\text{SCN}=26.05$.

Of all these values for $\cdot\text{SCN}$ the mean is 26.16, with a variation from the maximum and the minimum of -0.25 and $+0.21$ unit respectively. For the reason already mentioned, a slight correction is necessary in order to render this figure comparable with that obtained from the purely organic combinations—say, perhaps, 0.16 unit—this leaving a mean of about 26.0 as the refraction value of $\cdot\text{SCN}$ in "metallic" thiocyanates.

So great a discrepancy between this figure and the mean (23.3) determined for "organic" thiocyanates can scarcely be due to mere

* Recalculated from his experimental data.

errors of observation. Neither can it be attributed to the use of inaccurate values for the atomic refractions; for, if the numbers employed for sodium, calcium, and aluminium were each of them incorrect by as much as 10 per cent., either through deficiency or excess, the maximum error thereby caused in the values calculated for $\cdot\text{SCN}$ would in no case exceed a single unit.

Gladstone has observed (*loc. cit.*) that the mean atomic refraction of chlorine in organic derivatives is about 9.8 (line A), whereas in mineral chlorides the corresponding figure is about 10.7. In the case of bromine and of iodine the difference is still greater, the mean respective values being, for bromine, 15.3 and 16.9, and for iodine, 24.5 and 27.2. The amount of increase, it may be noted, shows a rough proportionality in each case to the atomic refraction of the radicle concerned; thus, $24.5 : 27.2 - 24.5 = 15.3 : 1.68$ (1.6 increase found by experiment); and $15.3 : 16.9 - 15.3 = 9.8 : 1.07$ (0.9 by experiment).

If for $\cdot\text{SCN}$ (ref. value = 23.3) a like influence should hold in its mineral combinations, the increased value, from analogy to the rise for iodine—the atomic refraction of which comes nearest—would be $\cdot\text{SCN} = 25.86$, or, roundly, 25.9, a figure but 0.1 unit removed from the approximate mean experimental value of 26.0 given above. From the chemical point of view, the thiocyanogen group presents a remarkably close analogy to the halogen radicles, and hence this apparent correspondence in respect of the physical property of molecular refraction is particularly interesting.

With a view to learn whether a similar variation is detectable in the case of other radicles, we have collected from various sources (mostly Gladstone, *Proc. Roy. Soc.*, 1867, **16**, 441; *Journ. Chem. Soc.*, 1870, **23**, 107; *Trans.*, 1884, **45**, 245; 1891, **59**, 595; also Landolt's *Tabellen*, etc.) the results incorporated in the following table. Not to encumber it with data already published, we have given merely the figures for the molecular refractions of the acidic residues, obtained by deducting from the molecular refraction of each compound the ordinary value of its basic constituent; the figures are here calculated in all cases for the solar line A.

Refraction Values of Acidic Radicles in conjunction with Organic and with Inorganic Radicles (line A).

		Mean.
<i>Nitrates, NO₃:</i>		
Organic.	14.7 (C ₂ H ₅)	14.70
Inorganic.	14.20 (Na, mean of 2); 14.10 (K, mean of 2); 14.85 (Ag)	14.29
<i>Nitrites, NO₂:</i>		
Organic.	11.9 (C ₄ H ₉)	11.90
Inorganic.	11.8 (K, mean of 5); 11.10 (Na, mean of 2).....	11.60

		Mean.
<i>Sulphates</i> , SO_4 :		
Organic.	18·69 (Me) ; 19·73 (Et)	18·71
Inorganic.	16·85 (K, mean of 5) ; 18·25 (Na, mean of 3) ; 16·86 (NH_4)	17·43
<i>Carbonates</i> , CO_3 :		
Organic.	12·9 (C_2H_5).....	12·90
Inorganic.	13·18 (Na, mean of 5) ; 12·84 (K, mean of 4) ...	13·01
<i>Cyanides</i> , CN :		
Organic.	9·06 (Et, mean of 3) ; 9·1 (C_4H_9) ; 9·1 (C_5H_{11})...	9·08
Inorganic.	9·30 (K, mean of 3)	9·30
<i>Oxalates</i> , C_2O_4 :		
Organic.	18·2 (C_2H_5) ; 20·4 (C_5H_{11})	19·30
Inorganic.	20·8 ($\text{H}_2\text{C}_2\text{O}_4$) ; 21·76 (K, mean of 2)	21·44
<i>Formates</i> , CHO_2 :		
Organic.	12·05 (C_5H_{11})	12·05
Inorganic.	12·0 (K, mean of 3) ; 12·15 (Na, mean of 3)	12·07
<i>Acetates</i> , $\text{C}_2\text{H}_3\text{O}_2$:		
Organic.	20·51 (Me) ; 19·72 (Et) ; 19·94 (Pr) ; 21·69 (C_5H_{11}) ; 19·66 (C_3H_5) ; 20·1 (PhC_2H_4) ; 19·45 (tolyl) ; 19·49 (cinnamyl)	20·07
Inorganic.	19·85 (K, mean of 2) ; 19·60 (Na) ; 19·12 (Ba) ; 19·76 (Ca) ; 20·28 (Pb) ; 19·55 (Mg)	19·71
<i>Benzoates</i> , $\text{C}_6\text{H}_5\cdot\text{CO}_2$:		
Organic.	55·0 (Me) ; 54·95 (Et)	54·97
Inorganic.	54·65 (K, very dilute solution)	54·65

Many of the discrepancies in the preceding table are doubtless more apparent than real. In five out of the nine groups, the "inorganic" combinations give for the acidic residue a lower value than do the "organic"; in the remaining four this order is reversed. The sum of the differences of the mean values for the various acid residues amounts, where the "inorganic" figure is the higher, to 2·49 units, and, where this figure is the lower, to 2·53 units. So far, therefore, as the gross result is concerned, there is little reason to suppose that the refraction value of the acid residues named above is dependent on whether they are conjoined with an organic or an inorganic group.

In detail, the same appears to hold to a large extent; for, in seven out of the nine sets compared—namely, for nitrates, nitrites, carbonates, cyanides, formates, acetates, and benzoates—the difference between the refraction values of an acid radicle in organic and in inorganic combination, respectively, does not in any case exceed 0·4 unit, and averages a bare quarter of a unit.

The case of the oxalates and of the sulphates is not in harmony with the preceding. As may be seen from the table, the values of the oxalic residue show discordance among themselves, alike in organic and in inorganic combinations, and the mean figures for each class differ considerably; amongst the sulphates there is a similar variation. We have no means of checking the correctness, or otherwise, of refraction values for the *A* line; but have endeavoured to determine experimentally whether variations of a like kind are noticeable with sodium light.

The molecular refractions observed were as follows (experimental details are given at the end of the paper):

<i>Potassium sulphate</i> , K_2SO_4 .	7 determinations.
Mean = 32·34. Variation, +0·44 to -0·61.	
<i>Sodium sulphate</i> , Na_2SO_4 .	5 determinations.
Mean = 26·2. Variation, +0·25 to -0·22.	
<i>Ammonium sulphate</i> , $(NH_4)_2SO_4$.	2 determinations.
Mean = 39·55. Variation, $\pm 0\cdot02$.	
<i>Potassium methyl sulphate</i> , $KMeSO_4$.	
$M_D = 34\cdot38$.	
<i>Potassium ethyl sulphate</i> , $KEtSO_4$.	3 determinations.
Mean = 42·10. Variation, +0·23 to -0·18.	
<i>Sodium ethyl sulphate</i> , $NaEtSO_4$.	3 determinations.
Mean = 38·72. Variation, +0·28 to -0·33.	
<i>Ethyl sulphate</i> , Et_2SO_4 .	2 determinations.
Mean = 52·23. Variation, $\pm 0\cdot01$.	

For the last ester Nasini and Costa obtained (*Pubbl. del Ist. chim. Roma*, 1891, 111) $M_D = 52\cdot47$ (interpolated).

By deducting from these results the atomic refractions given above, we find as the refraction values of the SO_4 group (line *D*) in the inorganic sulphates:

Potassium sulphate	16·54	
Sodium sulphate	17·40	Mean = 16·89
Ammonium sulphate	16·75	

Sodium sulphate gives for the SO_4 group a distinctly higher value than that obtained from the potassium or the ammonium salt corresponding. It seems probable that this is no accidental difference, due, for example, to variable hydration of the salt, for when the anhydrous compound was used (ignited in a platinum dish), the results were unchanged. It will be noticed, moreover, on reference to the table of refraction values of acidic radicles, pp. 930, 931, that, whilst the refraction of the SO_4 group is the same for potassium and for ammonium sulphate, in the case of sodium sulphate the increase is even greater than that which we have observed, namely, almost $1\frac{1}{2}$ units, instead of about $\frac{3}{4}$ of a unit.

Ethyl sulphate gives for the SO_4 group a markedly higher figure than the above mean of 16·89, the mean of all the values being 18·91. If the increased refraction effect of the sulphuric residue is conditioned through its being united to purely organic radicles, one might anticipate that if this group were conjoined at once with an inorganic and with an organic radicle, its refraction value would lie between the extremes, which, it would appear from the following results, is the case. Thus, M_D for SO_4 , as deduced from measurements of the metallic alkyl sulphates, is:

From potassium methyl sulphate	17·48	
„ „ ethyl „	17·50	Mean = 17·53
„ sodium „ „	17·62	

This mean falls a little below the arithmetic mean (17·90) of the two mean figures given.

Two oxalates were re-examined, namely, those containing ethyl and potassium respectively, the molecular refractions being as follows:

Ethyl oxalate	55·20 ; 55·24	Mean = 55·22
Potassium oxalate	37·58 ; 37·26	Mean = 37·42

Hence the refraction effect of the oxalic residue is:

From ethyl oxalate	$C_2O_4 = 21·82$
„ potassium oxalate	$C_2O_4 = 21·62$

As they differ by no more than a fifth of a unit, we regard these figures as practically indistinguishable.

So far, therefore, as may be judged at present, it would appear that the only cases in which the refraction value of an acidic residue is appreciably changed through its union with an inorganic radicle on the one hand, or with an organic on the other, are those of chlorides, bromides, iodides, thiocyanates, and sulphates. When the conjoined electropositive radicle is inorganic, the last-named give lower values than when it is organic; in the other four classes this effect is reversed.

Considering the marked chemical analogy subsisting between chlorides, bromides, iodides, thiocyanates, and cyanides, one might anticipate that the last-named would show in organic combinations a lower figure for the cyanogen residue than in metallic. From analogy to chlorine, the difference would be 0·8—0·9 unit, whereas the observed difference (for the *A* line) is little more than 0·2 unit; in other words, not distinctly appreciable. Nevertheless, it is by no means certain that such a difference as the former does not exist; for the only measurements at present available are those of a single compound, namely, potassium cyanide, and to obtain this salt, free from admixture, is a matter of some difficulty.

That the abnormally high refraction value of the halogens in mineral salts is not due to electrolytic dissociation may be inferred from the fact that various other salts which undergo this dissociation in presence of water give no higher values when dissolved in it than are obtained from their undissociated organic congeners; besides, as just pointed out, the reverse holds for the sulphates. In any case, positive evidence is forthcoming; that the molecular refraction of dissolved haloid inorganic salts is not perceptibly affected by the degree of concentration of their solutions may be judged from the following table, constructed from Bender's measurements of refractive index at about 19° (*Wied. Ann.*, 1890, **39**, 91); the corresponding densities being obtained from curves drawn from

the data given in Landolt's *Tabellen*. As before, not to load the paper with figures which are sufficiently accessible, we have given merely the end results:

Mol. Refraction of Certain Salts in Water at Different Concentrations.

Potassium bromide.		Sodium bromide.		Potassium iodide.	
Grams in 1000 c.c.	M_D .	Grams in 1000 c.c.	M_D .	Grams in 1000 c.c.	M_D .
118.84	25.48	102.76	21.35	165.62	36.32
237.68	25.23	205.52	21.60	331.24	35.60
356.52	25.35	308.28	22.02	496.86	36.20
		411.04	21.85	662.48	35.90
				828.10	35.82

Thus, at the greatest concentration, namely, five times the least, potassium iodide gives for M_D one-half unit lower; potassium bromide at treble concentration, 0.13 unit lower; sodium bromide at quadruple concentration, 0.5 unit higher; there is no regularity in the variation, and the maximum deviation of any figure from the mean of each set is about one-third of a unit. Such variation, unless the most extreme care be taken in every detail, is not greater than the experimental error attending measurements of the kind.

Whether the molecular refraction of halogen salts is changed by dissolution in water it is not easy to decide, their densities when in the solid state being influenced so greatly by the way in which they are prepared. Thus, for so well known a salt as sodium chloride, at temperatures from 0° to 17°, various observers have recorded densities from 2.05 to 2.204, this difference amounting to more than 7 per cent. of the total mean figure measured. Excluding 2.204, which is exceptionally high, the mean of all the other values is about 2.15, which would give for solid sodium chloride $M_D = 14.9$. For the same salt in aqueous solution, Schütt found (*Zeitsch. physikal. Chem.*, 1890, **5**, 358) $M_D = 15.9$, and Hallwachs (*Wied. Ann.*, 1894, **53**, 10), at concentrations varying from 14.6 to 0.305 grams per 100 c.c., $M_D = 15.8$, this being the mean of nine measurements, the maximum deviation of any one of which from this mean did not exceed 0.1 unit. Sodium chloride, therefore, appears to give in aqueous solution a molecular refraction higher by nearly one unit than when in the solid state.

It is possible, however, that this difference is more apparent than real, depending perhaps on some unknown accidental conditions. For, in the case of potassium bromide and of potassium iodide, it does not seem to exist: thus, for solid and for dissolved potassium bromide, $M_D = 25.45$ and 25.35 respectively, the corresponding experimental values for potassium iodide being 36.05 and 35.97.

Ammonium chloride, too, gives in the solid state $M_D = 22.57$, and, in aqueous solution, $M_D = 22.82$; for potassium chloride, the corresponding figures are about 18.4 and 18.5. The data on which these numbers are based are taken from the sources already mentioned.

To determine with great precision the molecular refractive power of solids is difficult, by reason of the considerable variations in physical state, which may occur in different specimens of a substance of fixed chemical composition. But, even allowing for this, it may safely be concluded that there is, at all events, no well-marked difference, so far as the above-named salts are concerned, between their molecular refractions, whether they are dissolved or not. It is plain, at least, that the increased values for bromine and for iodine in metallic salts, as compared with organic (1.6 and 2.7 units respectively), are not due solely to the dissolution of the compounds, seeing that, in the cases given, the figures for the dissolved salts are even a shade lower than those obtained from the solids. Besides, even if liquefaction by water, or dissociation by the solvent, could be connected with the higher values given by metallic haloid salts, the difficulty would now arise as to why many other acid residues are not similarly affected. Moreover, as we have shown above, in the case of the sulphates, the dissolved and partly dissociated metallic salt may give actually a lower relative value than the undissociated ester. There does not seem to be any connexion, as regards this variability of refractive power, between the "strengths" of the conjoined acid residues, relatively to one another, or, in like manner, between the effects of the various basic constituents, according as they are more or less electropositive. It is difficult to reconcile the facts, apparently so conflicting, with the hypothesis that molecular refraction is a simple additive property of matter.

Silicon Thiocyanate.

It has been shown in previous communications (Dixon, Trans., 1901, **79**, 541; 1904, **85**, 350; Dixon and Taylor, *ibid.*, 1908, **93**, 2148) that the so-called phosphorus thiocyanate, as well as the corresponding phosphoryl derivative, unite directly with bases, such as aniline or diphenylamine, to form additive compounds in which one, at least, of the conjoined rhodanide groups behaves distinctly as thiocarbimide; the molecular refraction, too, of both $P(CNS)_3$ and $PO(CNS)_3$ appears to support the view that these substances are thiocarbimides, at all events when in the static condition.

Silicon thiocyanate, on the other hand, has been subjected to a careful examination from the chemical point of view by Emerson Reynolds (Trans., 1906, **89**, 397), who concludes that it is entirely devoid of thiocarbimidic properties, and behaves exclusively as a

thiocyanate. Recently, having occasion to prepare this compound, we took the opportunity to examine it in the respect mentioned, applying for the purpose exactly the same treatment with nitrogenous bases, alkaline metallic solutions, and so on, as had been adopted with the phosphorus derivatives. Without giving the details of experimental methods that already have been described, we may state that the results corroborate entirely the conclusion of Reynolds, for in no case did we obtain from silicon thiocyanate the least indication of any tendency to behave as a thiocarbimide. It would have been interesting to determine the molecular refraction of so definitely marked a thiocyanate; but the specimen obtained was no more than approximately pure, and hence was unsuitable for the purpose. It is sometimes very difficult to judge from the reaction products of a strongly electronegative rhodanide what its statical constitution may be, for the failure of an acidic thiocarbimide to give the products characteristic of the $\cdot\text{NCS}$ group when this is conjoined with a hydrocarbon radicle is sometimes a mere matter of the conditions under which it is caused to interact. Thus, for example, acetylthiocarbimide, when placed in contact with aniline, may behave almost quantitatively as such, or some few hundredths only of its weight may enter into thiocarbamidic combination, the remainder decomposing as if the compound were acetyl thiocyanate (Dixon and Hawthorne, *Trans.*, 1906, **89**, 468; Hawthorne, *ibid.*, 556). Many other cases are known of indubitable thiocarbimides behaving, in certain circumstances, almost entirely as thiocyanates. Whilst, therefore, so far as its "reaction formula" is concerned, the experimental facts hitherto available point clearly enough to the view that silicon rhodanide is a true thiocyanate, it seems nevertheless by no means impossible that this substance, when in the static condition, may contain $\cdot\text{NCS}$ groups. This conjecture, however, is based solely on the grounds that most distinctly electronegative radicles appear to be incapable of forming thiocyanates in ordinary circumstances, and that the chemical behaviour as such, which they often display, is due to the feebleness of the union between the electronegative radicle and the rhodanide group. Thus, supposing that aniline, when presented to such a thiocarbimide, $\text{R}\cdot\text{NCS}$, tends to produce—or does, for the moment, actually produce—the thiocarbamide, $\text{R}\cdot\text{NH}\cdot\text{CS}\cdot\text{NHPh}$, the radicle, R , thereupon splitting off from the attached nitrogen atom, the formation of $\text{H}\cdot\text{NCS}$ and an anilide, $\text{R}\cdot\text{NHPh}$, is to be expected. The latter may, or may not, be stable; the former is unstable, and when liberated always changes into thiocyanic acid. In fact, since thiocyanates, as a rule, do not combine with aniline, this explanation may, perhaps, serve best to account for the observed facts. However

this may be, it is interesting to note that silicon thiocyanate is the only known rhodanide of a well-marked electronegative radicle which shows no tendency, in ordinary circumstances, to behave as a thiocarbimide.

The following table gives the experimental details from which

Molecular Refractions of Certain Sulphates and Oxalates.

Salt.	Mols. water to 1 of salt.	t° .	Solution.		M_D .	Value of SO_4 .	Material used.
			$dt^{\circ}/4^{\circ}$.	$\mu D/t^{\circ}$.			
K_2SO_4	90.9	14°	1.0779	1.34436	32.38	16.58	(i)
	99.2	15.5	1.0724	1.34361	32.11	16.31	(ii)
	99.39	10	1.0735	1.34394	31.90	16.10	(i)
	100.0	11	1.0727	1.34394	32.23	16.43	(i)
	100.0	17	1.0715	1.34344	32.20	16.40	(iv)
	100.53	14	1.0718	1.34402	32.95	17.15	(iv)
	107.4	14	1.0705	1.34372	32.63	16.83	(iii)
Na_2SO_4 ...	65.8	17	1.0984	1.34873	26.14	17.34	(ii)
	71.2	13.5	1.0938	1.34855	25.95	17.15	(iii)
	72.4	15	1.0872	1.34694	26.36	17.56	(iii)
	74.9	13.5	1.0884	1.34771	26.42	17.62	(ii)
	74.9	15	1.0880	1.34745	26.13	17.33	ignited in platinum
$(NH_4)_2SO_4$ {	11.06	16	1.2267	1.39275	39.57	16.77	(i)
	11.24	17	1.2259	1.39246	39.53	16.73	(ii)
$KEtSO_4$...	12.17	13	1.2315	1.37024	42.15	17.55	(i)
	12.17	14	1.2315	1.36960	41.87	17.27	(i)
	14.50	12	1.2033	1.36632	42.28	17.68	(v)
$NaEtSO_4$...	12.39	13.5	1.2380	1.37431	38.44	17.34	(i)
	16.71	12.5	1.1699	1.36360	38.67	17.57	(v)
	17.40	14	1.1689	1.36387	39.05	17.95	(vi)
$KMeSO_4$...	9.86	13.5	1.2914	1.36905	34.38	17.48	(i)
Et_2SO_4	—	13.5	1.1871	1.40250	52.22	18.82	(vii)
	—	15	1.1842	1.40171	52.24	18.84	(viii)
						Value of C_2O_4 .	
$K_2C_2O_4$...	27.77	17	1.1972	1.36723	37.26	21.46	Recrystallised from dilute alcohol.
	54.30	13.5	1.1111	1.35344	37.58	21.78	Do., Do.
$Et_2C_2O_4$...	—	17.5	1.0862	1.41098	55.24	21.84	B. p. 96°/30 mm.
	—	17.5	1.0871	1.41098	55.20	21.80	B. p. 97–99°/ 30 mm.

(i). Best material obtainable commercially.

(ii). Same, dried at 100°.

(iii). „ recrystallised from water.

(iv). „ „ „ „ and dried at 100°.

(v). „ „ „ „ alcohol and air-dried.

(vi). „ „ „ „ „ dried at 100°.

(vii). „ heated to 100° under diminished pressure.

(viii). „ distilled; b. p. 134.5°/12 mm.

the foregoing molecular refractions are calculated. It may be added that each set of measurements is the result of a separate, independent experiment; thus, for example, where salts were examined at different concentrations, the weaker solutions do not represent stronger ones diluted, but were made by direct weighing in each case.

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LXIX.—*The Action of Aromatic Amines on Ethyl Malonate.*

By FREDERICK DANIEL CHATTAWAY and JAMES MONTROSE DUNCAN
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THE action of aniline on ethyl malonate was first investigated by Freund (*Ber.*, 1884, **17**, 133), who, by heating the compounds together for many hours, obtained malonanilide. The other possible product of the action, ethyl malonanilate, either was not formed under the conditions of Freund's experiment, or more probably was overlooked on account of its low melting point.

Freund further isolated malonanilic acid from its calcium salt, which he obtained by heating phenylmalonamide with milk of lime, but was unable to convert it into an ethyl ester by the interaction of its silver salt and ethyl iodide.

Rügheimer (*Ber.*, 1884, **17**, 235) was equally unsuccessful in obtaining ethyl malonanilate from aniline and ethyl malonate. He found (*ibid.*, 736) that malonanilic acid could be more easily produced by heating together at 105° a mixture of aniline and malonic acid. The yield, however, in this method is not good, as the decomposition into carbon dioxide and acetanilide, which takes place quantitatively at 132°, goes on to some extent during the whole course of the heating.

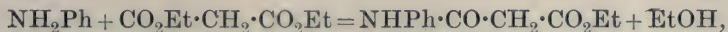
Ethyl malonanilate was first obtained by Rügheimer and Hoffmann (*Ber.*, 1884, **17**, 739) by the interaction of aniline and ethylmalonyl chloride. These chemists (*Ber.*, 1885, **18**, 2971) also prepared the malonotoluidic acids by heating the corresponding toluidines with malonic acid, and converted them into their ethyl esters by saturating alcoholic solutions with hydrogen chloride.

Malonanilic acid has also been obtained in small quantity by Seifert (*Ber.*, 1885, **18**, 1358) in an extremely interesting intra-

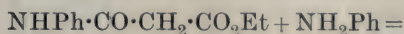
molecular rearrangement of phenylacetylcarbamate, which occurs at a somewhat elevated temperature.

These researches leave the impression that ethyl malonanilate is only to be obtained with some difficulty, and that it is not formed by the action of malonic ester on aniline.

The recent work of Chattaway and Mason (this vol., p. 341), which has shown that the action of ethyl malonate on halogen substituted anilines follows a perfectly regular course, and that both substituted ethylmalonanilates and substituted malonanilides are formed, made it appear probable that unsubstituted aromatic amines would act similarly, and that the malonanilic esters and malonanilides formed would be easily separable owing to their widely differing solubilities. This conclusion has now been confirmed. When aniline or any aromatic amine is heated with ethyl malonate, one only of the CO_2Et groups of the latter reacts at first, for example:



the ester thus formed being converted into the anilide by further action of the amine, for example:



The corresponding acids can be obtained by hydrolysing the esters with a dilute solution of sodium carbonate, a procedure which is by far the simplest method of preparing them.

EXPERIMENTAL.

Action of Aniline on Ethyl Malonate and Preparation of Malonanilic Acid.

A mixture of 10 grams of aniline (1 mol.) and 25 grams of ethyl malonate (1.5 mols.) was heated to gentle ebullition for thirty minutes in a flask attached to an air condenser, of such a length that the alcohol formed escaped while the malonic ester flowed back into the flask. The product was then mixed with twice its bulk of alcohol and allowed to cool, when malonanilide, $\text{NHPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{NHPh}$ (7 grams), crystallised out. The filtrate was poured into excess of water and well shaken, when ethyl malonanilate, $\text{NHPh} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$ (10.5 grams), separated as an oil, which slowly solidified. The whole of the aniline is thus converted into malonanilide and ethyl malonanilate. The yield of the latter can be increased at the expense of the former if a larger quantity of ethyl malonate is used, but the ester is then brought to crystallisation with less ease.

Ethyl malonanilate can with some difficulty be recrystallised from dilute alcohol.

To prepare malonanilic acid, the filtrate, in a second experiment carried out precisely as described above, was added to a solution of 8 grams of sodium carbonate in 100 c.c. of water, and steam was blown through the mixture for about an hour until the ester, which at first separated as an oil, had completely disappeared. The cooled liquid was then filtered from a slight turbidity, due to a trace of malonanilide dissolved by the alcohol, and hydrochloric acid was added in slight excess. Malonanilic acid, $\text{NHPH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$ (8 grams), quickly crystallised out in colourless prisms, which melted and completely decomposed at about 132° , yielding carbon dioxide and acetanilide. The ester is seen to be thus hydrolysed practically quantitatively by this procedure, which is by far the simplest method of preparing malonanilic acid.

*Preparation of Malono-*p*-toluidic Acid.*

A mixture of 11 grams of *p*-toluidine (1 mol.) and 25 grams of ethyl malonate (1.5 mols.) was heated as described above to gentle boiling for thirty minutes. The product, which solidified on cooling, was mixed with 100 c.c. of warm alcohol, and the malono-*p*-toluidide (m. p. 259°), which is very sparingly soluble in alcohol, was collected. A yield of 8 grams of this compound was obtained. The remainder of the *p*-toluidine was converted into ethyl malono-*p*-toluidate (m. p. 86°), which separated as a colourless, crystalline mass (10 grams) when the filtrate from the malono-*p*-toluidide was poured into water.

Malono-*p*-toluidic acid is obtained quantitatively when ethyl malono-*p*-toluidate is hydrolysed as described previously. For this purpose it is not necessary to use the pure ester; the filtrate from the malono-*p*-toluidide can be directly employed. The alcohol distils off immediately the steam is passed, and any traces of malono-*p*-toluidide dissolved by the alcohol are not acted on by the alkaline carbonate, and may be filtered off when the saponification is complete. On adding concentrated hydrochloric acid in slight excess to the clear solution of the sodium salt, malono-*p*-toluidic acid separates in colourless prisms. These can be recrystallised from water, in which they are sparingly soluble, or from alcohol, in which they are more readily soluble.

Preparation of Malono-o-toluidic Acid.

A mixture of 11 grams of *o*-toluidine and 25 grams of ethyl malonate was gently boiled for thirty minutes; 60 c.c. of alcohol were then added to the warm product, when malono-*o*-toluidide (m. p. 198°) slowly crystallised out (9 grams). After collecting this compound, the ethyl malono-*o*-toluidate, into which the remainder of the *o*-toluidine had been converted, was obtained as a colourless, crystalline mass (8.5 grams) by pouring the filtrate into water.

This ester gave a quantitative yield of sodium malono-*o*-toluidate on being hydrolysed in the manner previously described. On adding hydrochloric acid to the solution of the sodium salt, malono-*o*-toluidic acid separated in colourless prisms.

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LXX.—*Syntheses of p-Hydroxyphenylethylalkylamines.*

By GEORGE STANLEY WALPOLE.

THE methylamino- and ethylamino-homologues of *p*-hydroxyphenylethylamine have been prepared in order that their physiological properties might be examined and compared with those of allied compounds.

p-Hydroxyphenylethylmethylamine, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHMe}$, is of particular interest, in that it stands in the same relationship to methyltyrosine as does *p*-hydroxyphenylethylamine to tyrosine. The crystalline form, melting point, and platinum content of the platinum-chloride of this substance have been found to agree with the data given by Blau (*Zeitsch. physiol. Chem.*, 1908, **58**, 153) for the corresponding compound prepared from the base obtained by the destructive distillation of surinamine. There is no longer room for doubt, therefore, that the latter substance is, as supposed, methyltyrosine.

No attempt was made to obtain it by the direct methylation of *p*-hydroxyphenylethylamine since Barger (*Trans.*, 1909, **95**, 2195) and, later, Rosenmund (*Ber.*, 1910, **43**, 305) have drawn attention to the difficulty of isolating products intermediate between this substance and hordenine methiodide. The method first adopted was suggested by the process employed by Hepp (*Ber.*, 1877, **10**,

328) for the preparation of methylaniline. The starting point was *p*-methoxyphenylethylamine, prepared from anisaldehyde by the method described by Barger and the author.

The acetyl derivative of this was prepared, and methylation of the imino-group brought about in dry xylene solution by metallic sodium followed by methyl iodide. The product, on hydrolysis, gave acetyl-*p*-hydroxyphenylethylmethylamine and *p*-hydroxyphenylethylmethylamine.

While the investigation of the hydrolysis of acetyl-*p*-methoxyphenylethylmethylamine was in progress, a paper by Johnson and Guest (*Amer. Chem. J.*, 1909, **42**, 340) describing the monomethylation of phenylethylamine was published. The preparation of *benzenesulphonyl-p-methoxyphenylethylmethylamine* on lines suggested by their preparation of *benzenesulphonylphenylethylmethylamine* was carried out, and this substance gave, on partial hydrolysis, *benzenesulphonyl-p-hydroxyphenylethylmethylamine*, and on complete hydrolysis, *p*-hydroxyphenylethylmethylamine. The synthesis of the corresponding ethylamino-base was accomplished in a similar manner.

EXPERIMENTAL.

Synthesis of p-Hydroxyphenylethylmethylamine from p-Methoxyphenylethylamine.

The steps involved in obtaining *p*-methoxyphenylethylamine from anisaldehyde through *p*-methoxyphenylpropionic acid have been already described (*Trans.*, 1909, **95**, 1720). In later preparations the conditions under which the last step (Hofmann's reaction) was carried out were altered slightly, with the result that the yield of amine from amide was considerably increased. To a cold solution of 31 grams of potassium hydroxide in 120 c.c. of water, 5.3 c.c. of bromine were added. The amide (18 grams) was finely powdered and rubbed to a cream with a little water, and then washed rapidly with 200 c.c. of water into the hypobromite solution. The mixture was maintained at 55° for one hour, then cooled, and extracted with ether. The ethereal extracts after filtration and evaporation on the water-bath left a residue which, when fractionated under 20 mm. pressure, yielded 7.5—8.5 grams of the amine, boiling at 138—142°, and a crystalline residue of higher boiling point. This consisted largely of a substance melting at 127°, which was probably the *isocyanate*, since, on hydrolysis with strong aqueous potassium hydroxide, it yielded more amine. The residues were therefore collected and converted separately into the amine.

Acetyl-p-methoxyphenylethylamine, $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NHAc}$.

7.8 Grams of *p*-methoxyphenylethylamine, dissolved in 15 c.c. of acetic anhydride, were boiled with 5 grams of anhydrous sodium acetate for four hours in an oil-bath under an air condenser fitted with a drying tube. The mixture was poured into boiling water, allowed to cool, and extracted with ether. The extract was washed with sodium carbonate solution to remove acid, dried, and fractionated. The yield of acetyl derivative, boiling at $195\text{--}200^\circ/15\text{ mm.}$, was 9.85 grams. It is a colourless, oily liquid, insoluble in water, but readily miscible in all proportions with alcohol, ether, xylene, benzene, etc.

Acetyl-p-methoxyphenylethylmethylaniline,
 $\text{MeO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMeAc}$.

To 9.85 grams of the above acetyl derivative, dissolved in 25 c.c. of dry xylene, 0.97 gram of sodium was added, and the flask heated under an air condenser in an oil-bath until the xylene boiled. The solution of the sodium, except 0.02 gram, was complete in twenty minutes. When still warm, the small remaining bead of sodium was removed, and a large excess, 8 c.c., of methyl iodide added. Sodium iodide separated rapidly, there was considerable evolution of heat, and after a few minutes' further warming, the reaction was considered complete. From the product after dilution with ether, sodium iodide was removed by extraction with water. The xylene-ether layer was dried and fractionated, yielding 5.25 grams of a colourless, oily liquid similar in its solubility relationships to the acetyl derivative. It was crystalline, but this property could not be used as a means of further purification. The oil boiled at $205\text{--}208^\circ/18\text{ mm.}$:

0.1560 gave 0.3979 CO_2 and 0.1168 H_2O . $\text{C} = 69.5$; $\text{H} = 8.3$.

$\text{C}_{12}\text{H}_{17}\text{O}_2\text{N}$ requires $\text{C} = 69.6$; $\text{H} = 8.2$ per cent.

Acetyl-p-hydroxyphenylethylmethylaniline,
 $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMeAc}$.

The oil just described (5.25 c.c.) was boiled for twenty minutes with 15 c.c. of hydriodic acid (D 1.70), the excess of acid removed on a water-bath under diminished pressure, and the residue dissolved in water. From the ethereal extracts a crystalline substance, melting at 142° , was obtained. In a later experiment colourless

hydriodic acid was used, and the hydrolysis conducted in a stream of carbon dioxide. This alteration in procedure, together with the substitution of amyl alcohol for ether as an extracting agent, had the effect of slightly facilitating the separation of this substance. The residue from the evaporation of the extracts was extracted in its turn with successive small quantities of boiling toluene, and after some time these deposited aggregates of white needles, which were washed with dry ether, and of which small samples were recrystallised from ethyl alcohol, methyl alcohol, and ethyl acetate. From these solvents the substance very slowly crystallises in small, isolated hexagonal plates, although from aqueous solution by slow evaporation in a vacuum desiccator, thin, colourless, spear-shaped needles are obtained. All the purified samples melted at 142° :

0.1547 gave 0.3856 CO_2 and 0.1092 H_2O . $\text{C}=67.98$; $\text{H}=7.84$.

$\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{C}=68.38$; $\text{H}=7.77$ per cent.

($\text{C}_{10}\text{H}_{13}\text{O}_2\text{N}$ „ $\text{C}=67.00$; $\text{H}=7.76$ „)

A minute quantity of the purified material gives Millon's reaction. It dissolves slowly in a small quantity of water or sodium carbonate solution, but instantly in aqueous sodium hydroxide. Its aqueous solution gives a heavy precipitate with phosphotungstic acid. From an attempted hydrolysis, by heating with 10 per cent. alcoholic potash for two hours on the water-bath, some of the material was recovered unaltered. 0.08 Gram was heated at 170° for two hours with 2 c.c. of concentrated hydrochloric acid, and then evaporated to dryness in a vacuum desiccator. The small residue was crystallised from alcohol by cautious addition of dry ether yielding 0.05 gram of slender, slightly coloured scales. The melting point of this substance and its benzoyl derivative, its crystalline form, and its physiological action were examined. A comparison with equal quantities of the hydrochlorides of *p*-hydroxyphenylethylamine and *p*-hydroxyphenylethylmethylaniline showed that these crystals consisted of the latter substance. In view of these facts, it is suggested that the compound melting at 142° has the constitution $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMeAc}$.

p-Hydroxyphenylethylmethylaniline, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NHMe}$.

4.43 Grams of acetyl-*p*-methoxyphenylethylmethylaniline were heated with 12 c.c. of concentrated hydrochloric acid at 165° for two hours. The excess of acid was removed by distillation under diminished pressure on the water-bath, and an aqueous solution of the residue was extracted completely with amyl alcohol. Over and above that amount required for neutralisation, 4 grams of sodium hydroxide were then added to the aqueous solution. Two extrac-

tions with the same solvent were made with the object of removing any base not phenolic, and finally the liquid was again neutralised, and in it were dissolved 6 grams of hydrated sodium carbonate. Four extractions with 20 c.c. of amyl alcohol sufficed to remove nearly all the phenolic base. The residue, on evaporation of these extracts, was crystallised from boiling xylene. The substance sought, still impure, separated in oily drops, which soon resolved themselves into fine needles, melting at $114-116^{\circ}$, of which 1.4 grams were collected.

Distillation under diminished pressure yielded 1.09 grams of material, boiling at $183-185^{\circ}/9$ mm., which solidified at once in the condenser. From a concentrated solution in hot alcohol it slowly separated, on cooling, in bundles of colourless, four-sided prisms, melting sharply at 130° :

0.1449 gave 0.3783 CO_2 and 0.1124 H_2O . $\text{C}=71.2$; $\text{H}=8.61$.

$\text{C}_9\text{H}_{13}\text{ON}$ requires $\text{C}=71.5$; $\text{H}=8.6$ per cent.

It is moderately soluble in water or sodium carbonate solution, and instantly dissolves in dilute acid or sodium hydroxide. It reddens phenolphthalein, gives Millon's reaction very intensely, reduces acid potassium permanganate in the cold, and may be precipitated by addition of excess of ammonia to an aqueous solution of a salt.

The *hydrochloride* is extremely soluble in water or alcohol. 0.2 Gram of the pure base was dissolved in a few drops of alcoholic hydrochloric acid. Slender, colourless scales, melting at 148.5° , separated on the addition of ether. They did not gain weight on exposure to the air for half an hour, and were recrystallised from alcohol and ether for analysis:

0.1391 gave 0.1059 AgCl . $\text{Cl}=18.8$.

$\text{C}_9\text{H}_{13}\text{ON}, \text{HCl}$ requires $\text{Cl}=18.9$ per cent.

The *platinichloride*, obtained by adding platinic chloride solution to a solution of the pure base in dilute hydrochloric acid, separates, after some time, in yellow needles. These melt and decompose at 205° (corr.), and correspond in this respect with the *platinichloride* of the base from surinamine described by Blau, the melting point of which is given as 205° :

0.0756 gave 0.0209 Pt . $\text{Pt}=27.6$.

$(\text{C}_9\text{H}_{13}\text{ON})_2\text{H}_2\text{PtCl}_6$ requires $\text{Pt}=27.3$ per cent.

Methylation to Hordenine Methiodide.—This procedure was initiated in order to confirm the constitution of the substance and its relation to the allied base hordenine. 0.1 Gram of the pure base, dissolved in a few drops of methyl alcohol, were warmed for a few minutes with 3 c.c. of methyl iodide. On cooling, long

needles of hordenine methiodide separated. They were recrystallised from water, when they melted at 229° , which is the melting point of hordenine methiodide. A mixture of equal weights of the two substances melted also at 229° .

A *dibenzoyl* derivative, prepared by the Schotten-Baumann method, was found to be very soluble in alcohol (0.3 gram in 0.5 c.c.), from which it crystallised on cautious dilution with water from time to time. Recrystallisation twice repeated from benzene and light petroleum yielded it in a pure condition in rosettes of colourless prisms, melting at 99° . From 0.40 gram of base, 0.28 gram of pure dibenzoyl derivative was obtained:

0.1510 gave 0.4260 CO_2 and 0.0808 H_2O . $\text{C}=76.94$; $\text{H}=5.94$.

0.1062 ,, 3.3 c.c. N_2 (moist) at 14° and 747 mm. $\text{N}=3.6$.

$\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=76.88$; $\text{H}=5.84$; $\text{N}=3.9$ per cent.

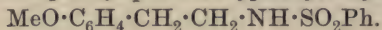
The *hydrogen oxalate*, prepared by pouring an alcoholic solution of the base into a saturated solution of oxalic acid in dry ether, was found to be very insoluble in absolute alcohol even at the boiling point. It melts and decomposes at 250° (uncorr.), and crystallises from alcohol in colourless needles.

The *picrate* melts at 149° .

A yellow *picrolonate*, extremely insoluble in water, was obtained by mixing aqueous solutions of picrolonic acid and the hydrochloride of the base. It melts and decomposes at $234\text{--}235^{\circ}$.

An alternative synthesis on similar lines to that described was performed. The benzenesulphonyl group, however, instead of the acetyl group, was attached to the nitrogen atom through all the stages up to the final hydrolysis.

Benzenesulphonyl-p-methoxyphenylethylamine,



9.23 Grams of benzenesulphonyl chloride and 7.9 grams of *p*-methoxyphenylethylamine were mixed with 70 c.c. of benzene. The mixture became warm, and after a minute 4.40 grams of potassium hydroxide in 30 c.c. of water were added, and the whole was shaken vigorously. The benzene layer which separated was dried and concentrated on the water-bath. On cooling, a mass of crystals separated, which could readily be obtained in the pure condition by recrystallisation from alcohol or benzene and light petroleum. The yield of purified material, which melted at $79\text{--}80^{\circ}$, was 15.5 grams:

0.1277 gave 5.6 c.c. N_2 (moist) at 14° and 746 mm. $\text{N}=5.0$.

$\text{C}_{15}\text{H}_{17}\text{O}_3\text{NS}$ requires $\text{N}=4.9$ per cent.

Methylation of Benzenesulphonyl-p-methoxyphenylethylamine and Hydrolysis of the Product.

To a solution in alcohol of 10 grams of the benzenesulphonyl derivative, prepared as described above, 2 grams of sodium hydroxide dissolved in a little water were added, and then 7 grams of methyl iodide. To ensure the completion of the reaction, the mixture was heated on the water-bath for fifteen minutes. The alcohol was then expelled, and the residue shaken with ether and water. The ethereal layer, on evaporation, left a clear, yellow oil.

7.3 Grams of this oil were heated with 10 c.c. of concentrated hydrochloric acid at 130—150° for two hours in a sealed tube. The excess of hydrochloric acid was then removed by evaporation in a vacuum, and the residue, a viscous liquid, was dissolved in 30 c.c. of water, and the solution extracted completely by shaking six times with 10 c.c. of amyl alcohol. The residue obtained from these extracts crystallised on cooling (A).

The aqueous layer was now neutralised, and a solution containing 5 grams of sodium hydroxide added. Three extractions with 10 c.c. of amyl alcohol yielded very little material, indicating that only a small quantity of non-phenolic base was present. The solution was again neutralised, 8 grams of hydrated sodium carbonate dissolved in it, and it was then completely extracted with ten portions of 15 c.c. of amyl alcohol. The extracts, after washing with a little sodium carbonate solution and filtering, gave, on evaporation, a residue (B).

Benzenesulphonyl-p-hydroxyphenylethylmethylamine,
 $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{SO}_2\text{Ph}.$

The residue (A) was extracted with ether, leaving 4 grams of a highly crystalline material. Boiling with animal charcoal in alcoholic solution removed a purple colouring matter accompanying this substance, and the subsequent addition of ether caused it to separate in white leaflets, melting at 133.5°. It is readily soluble in water, and a minute quantity of the pure material gives Millon's reaction:

0.2161 gave 8.7 c.c. N_2 (moist) at 15° and 760 mm. $\text{N}=4.71.$

0.1704 „ 0.1375 BaSO_4 . $\text{S}=11.09.$

$\text{C}_{15}\text{H}_{17}\text{O}_3\text{NS}$ requires $\text{N}=4.81$; $\text{S}=10.99$ per cent.

The residue (B) was extracted with boiling xylene, from which, on cooling, needles, melting at 123°, separated. These were washed with a little ether, and gave on distillation 0.4 gram of pure *p*-hydroxyphenylethylamine. From further extracts another 0.2 gram was obtained.

Under the above conditions, therefore, hydrolysis of benzenesulphonyl-*p*-methoxyphenylethylamine is not complete. Some phenolic secondary amine is obtained, and a considerable quantity of the intermediate product, benzenesulphonyl-*p*-hydroxyphenylethylmethylamine.

A second hydrolysis conducted in the same manner, except that the temperature was maintained at 170°, gave scarcely any of the intermediate product, the yield of pure base from 5 grams of benzenesulphonyl-*p*-methoxyphenylethylamine being nearly 1 gram.

Three grams of pure benzenesulphonyl-*p*-hydroxyphenylethylmethylamine also gave about a gram of *p*-hydroxyphenylethylmethylamine on hydrolysis with concentrated hydrochloric acid for two hours.

*Synthesis of p-Hydroxyphenylethylethylamine from
p-Methoxyphenylethylamine.*

This synthesis was conducted through the benzenesulphonyl derivative of *p*-methoxyphenylethylamine in a manner analogous to that described for the methyl base, methyl iodide being replaced by ethyl iodide. No attempt was made to isolate the intermediate phenolic benzenesulphonyl compound, and the hydrolysis was therefore conducted at 170°. Commencing with 6.9 grams of benzenesulphonyl-*p*-methoxyphenylethylamine, it was found possible to isolate 0.9 gram of the hydrochloride of the ethylamino-base. A slight modification of technique was necessitated in the later stages of this preparation, as it was found impossible to obtain the free base in the crystalline condition from xylene. The residue from the amyl-alcoholic extracts containing the ethylamino-phenolic base was therefore dissolved in 10 c.c. of amyl alcohol, and thoroughly shaken with dilute hydrochloric acid. The acid extracts were boiled with a small quantity of animal charcoal, filtered, and evaporated to dryness in a vacuum at the ordinary temperature. Needles up to 2 cm. in length of the nearly pure *hydrochloride* were thus obtained. These melted at 184—185°, and were not so extremely soluble in alcohol as the hydrochloride of the methyl homologue. On dilution with ether, the alcoholic solution deposited the hydrochloride in colourless needles. These, when dry, were found to be tinted very faintly pink, and not hygroscopic. Recrystallisation did not alter the melting point, but removed the colour:

0.0872 gave 0.0612 AgCl. Cl=17.3.

0.1161 „ 7.0 c.c. N₂ (moist) at 12° and 743 mm. N=6.9.

C₁₀H₁₅ON, HCl requires Cl=17.1; N=6.9 per cent.

The free base liberated from the hydrochloride by sodium

carbonate and extracted by means of amyl alcohol was distilled. It crystallised in the receiver, but the amount of material was insufficient to draw any accurate conclusion as to its boiling point, which, however, appeared to be $185\text{--}187^{\circ}/9\text{ mm.}$ It crystallised from alcohol in rosettes of colourless needles, melting at $157\text{--}158^{\circ}$.

A *picrolonate*, very insoluble even in boiling water, was formed by adding an aqueous solution of the purified hydrochloride to a cold saturated solution of picrolonic acid. It melts and decomposes at 216° , and this melting point remained unchanged even after repeatedly boiling the substance with water.

No platinichloride could be obtained. The residue left after careful evaporation of the mixed aqueous solution of platinic chloride and the hydrochloride of the base was instantly soluble in cold water and concentrated hydrochloric acid. This suggests a ready means of separating the ethyl base from its methyl homologue.

An alcoholic solution of the free base added to a saturated solution of oxalic acid in ether gave a cloudy precipitate of the *hydrogen oxalate*, which crystallised from alcohol in colourless, rhombic plates, melting and decomposing at 245° . This salt is much more soluble in alcohol than that of the corresponding methyl compound.

Dr. H. H. Dale has examined the physiological properties of the two bases described. The methylamino-base is almost, but not quite, as active as *p*-hydroxyphenylethylamine, whilst the ethylamino-base is considerably less active than either.

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LXXI.—*Preparation of the Acyl Derivatives of the Aldehyde-cyanohydrins. Part II.*

By OLIVER CHARLES MINTY DAVIS.

IN a previous communication (Trans., 1909, 95, 1403) a method was described for the preparation of acyl derivatives of aldehyde-cyanohydrins, which consisted in shaking an aqueous solution of potassium cyanide with the required aldehyde, and gradually adding the acid chloride to the cooled mixture.

With one exception the compounds investigated were derived from aromatic aldehydes, and further experiments have been carried out with those of the aliphatic series. The reaction has been found

to be quite general with these aldehydes, and theoretical yields of the compounds in question have been obtained by the action of benzoyl chloride on acetaldehyde, *isovaleraldehyde*, and heptaldehyde. In each case the resulting acyl derivatives are oils of high boiling point, which can be distilled without decomposition under diminished pressure.

An attempt was also made to carry out the reaction with acid chlorides of the aliphatic series, but although small amounts of the corresponding acyl derivatives are formed, they are not sufficiently stable to be isolated in a state of purity.

A number of corresponding experiments were then carried out with aliphatic and aromatic ketones, but with the exception of acetone it was not found possible to isolate the desired derivatives.

A series of investigations was made to determine the action of different reagents on the acylaldehyde-cyanohydrins. When dissolved in absolute alcohol and saturated with ammonia gas, the main reaction consists in the elimination of the acyl group with formation of the amide, which is invariably contaminated with oily matter.

On boiling with an aqueous solution of potassium hydroxide, all these compounds lose the acyl group with the formation of the potassium salt and liberation of the cyanohydrin, the latter, in presence of the alkali, giving rise to potassium cyanide and the corresponding aldehyde, which in several cases undergoes condensation.

Towards hydrochloric acid these compounds are fairly stable, but are decomposed when heated with this reagent in sealed tubes at 100—110°.

Only one derivative was fully investigated, namely, carbethoxymandelonitrile, which gave mandelamide after heating for a short time, but further heating gave rise to a mixture of mandelic acid and its ester.

EXPERIMENTAL.

Benzoyl-lactonitrile, $\text{BzO} \cdot \text{CHMe} \cdot \text{CN}$.

This was prepared by the interaction of acetaldehyde, aqueous potassium cyanide, and benzoyl chloride. The heavy oil which separated was extracted with ether, the ethereal solution washed with dilute potassium hydroxide solution, and dried. After removing the ether, a good yield of oil was obtained, which could be distilled without decomposition, even under the ordinary pressure. It boils at 198—200°/125 mm. or 269—270°/760 mm.:

0.4274 gave 29.4 c.c. N_2 (moist) at 16° and 758 mm. $\text{N} = 7.99$.

$\text{C}_{10}\text{H}_9\text{O}_2\text{N}$ requires $\text{N} = 8.00$ per cent.

α -Benzoyloxyisohexonitrile, $\text{CHMe}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This was obtained in the same manner as the compound just described by the interaction of aqueous potassium cyanide, *iso*-valeraldehyde, and benzoyl chloride. It is an almost colourless oil, boiling at $247\text{--}250^\circ/200$ mm.:

0.5284 gave 29.4 c.c. N_2 (moist) at 20° and 761 mm. $\text{N} = 6.37$.

$\text{C}_{13}\text{H}_{15}\text{O}_2\text{N}$ requires $\text{N} = 6.45$ per cent.

 α -Benzoyloxyoctonitrile, $\text{CH}_3 \cdot [\text{CH}_2]_5 \cdot \text{CH}(\text{OBz}) \cdot \text{CN}$.

This compound was prepared from heptaldehyde and benzoyl chloride; it is a colourless oil, boiling at $256\text{--}257^\circ/110$ mm.:

0.501 gave 24.6 c.c. N_2 (moist) at 15° and 757 mm. $\text{N} = 5.72$.

$\text{C}_{15}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{N} = 5.71$ per cent.

Benzoyloxyisobutyronitrile, $\text{BzO} \cdot \text{CMe}_2 \cdot \text{CN}$.

Prepared from acetone and benzoyl chloride in the presence of aqueous potassium cyanide. A very small yield of colourless oil, boiling at $185\text{--}190^\circ/70\text{--}80$ mm., was obtained after extracting with ether and drying. After several days the oil solidified to a mass of colourless, crystalline plates, melting at $35\text{--}36^\circ$:

0.6005 gave 37.4 c.c. N_2 (moist) at 16° and 755 mm. $\text{N} = 7.2$.

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{N}$ requires $\text{N} = 7.4$ per cent.

m-Nitrobenzoyloxyisobutyronitrile.

Prepared from *m*-nitrobenzoyl chloride, acetone, and potassium cyanide. A good yield of pale yellow crystals was obtained, and, after recrystallisation from alcohol, these melted at $75\text{--}76^\circ$:

0.214 gave 23.00 c.c. N_2 (moist) at 17° and 749 mm. $\text{N} = 12.2$.

$\text{C}_{11}\text{H}_{10}\text{O}_4\text{N}_2$ requires $\text{N} = 11.9$ per cent.

Ethyl-carbonatoisobutyronitrile, $\text{CO}_2\text{Et} \cdot \text{O} \cdot \text{CMe}_2 \cdot \text{CN}$.

A very small yield of this derivative was obtained by the interaction of acetone, aqueous potassium cyanide, and ethyl chloroformate. It is a colourless oil, boiling at $140\text{--}142^\circ/100$ mm.:

0.332 gave 26.6 c.c. N_2 (moist) at 21° and 765 mm. $\text{N} = 9.1$.

$\text{C}_7\text{H}_{11}\text{O}_3\text{N}$ requires $\text{N} = 8.91$ per cent.

Action of Butyryl Chloride on Benzaldehyde in presence of Aqueous Potassium Cyanide.

In this reaction a very small yield of an oil was obtained, which boiled at $200^{\circ}/80$ mm. It appeared to be partly decomposed during distillation. An analysis showed it to be in all probability impure butyrylmandelonitrile:

0.2207 gave 0.561 CO_2 and 0.130 H_2O . $\text{C} = 69.3$; $\text{H} = 6.5$.

$\text{C}_{12}\text{H}_{13}\text{O}_2\text{N}$ requires $\text{C} = 70.9$; $\text{H} = 6.4$ per cent.

Reactions of Acylaldehyde-cyanohydrins: Action of Ammonia.

Benzoylmandelonitrile.—Five grams of this nitrile were dissolved in absolute alcohol, and the solution saturated with ammonia. After twelve hours the solution was evaporated, when a crystalline solid, mixed with oily matter, was obtained. When crystallised from benzene, the substance melted at 127° , and its reactions and analysis showed it to consist of benzamide.

Benzoyl-p-methoxymandelonitrile and Benzoyl-lactonitrile.—When treated with ammonia, as described above, both these compounds gave benzamide.

Cinnamoylmandelonitrile.—In this case the reaction product was contaminated with a considerable amount of resinous matter, and only a small amount of cinnamide could be isolated.

Action of Hydrochloric Acid on Carbethoxymandelonitrile.

A small quantity of the above substance was heated in a sealed tube for one and a-half hours at 110° . When cool, there was considerable pressure in the tube, and colourless crystals had separated, which, after crystallisation from alcohol, melted at 134 – 135° , and gave the reactions of mandelamide.

In a second experiment the heating was prolonged for five hours, when ammonium chloride was found to be present in almost theoretical amount. In addition, mandelic acid and its ester were identified, the latter giving mandelic acid on hydrolysis with potassium hydroxide.

Action of Potassium Hydroxide.

Benzoylmandelonitrile.—Five grams of the compound, crystallised from alcohol, were heated under a reflux condenser for five hours with 10 c.c. of 15 per cent. aqueous potassium hydroxide. On cooling, the product was extracted with ether, and 2.5 grams of an oil were obtained, which solidified after some time. On crystallisation, first from alcohol and finally from boiling water, it

melted at 134° , and analysis showed it to be benzoin. The residue was distilled in a current of steam, and the distillate contained traces of ammonia and some benzaldehyde.

After removal of the benzaldehyde, the liquid remaining was found to contain potassium cyanide, and on acidifying with dilute hydrochloric acid, benzoic acid was precipitated.

Several similar experiments were made, and it appears that the proportion of benzoin to benzaldehyde formed depends on the concentration of the potassium hydroxide solution.

Benzoyl-p-tolylglycollonitrile.—When treated as described in the previous case, 5 grams of benzoyl-*p*-tolylglycollonitrile gave 2.5 grams of a compound, which corresponded very closely with the benzoyl derivative of *p*-toluoin, and not to *p*-toluoin, as was expected. After crystallisation from alcohol it melted at $122\text{--}123^{\circ}$ (Beilstein gives the melting point of benzoyl-*p*-toluoin as 119° , whereas *p*-toluoin melts at $88\text{--}89^{\circ}$). The analysis leaves little doubt that the substance is actually benzoyl-*p*-toluoin, but it is not easy to see how it is formed in this reaction:

0.1980 gave 0.5822 CO_2 and 0.1066 H_2O . $\text{C}=80.15$; $\text{H}=5.9$.

0.510, in 24.87 benzene, gave $\text{E}=0.155^{\circ}$. $\text{M.W.}=353$.

$\text{C}_{23}\text{H}_{20}\text{O}_3$ requires $\text{C}=80.23$; $\text{H}=5.8$ per cent. $\text{M.W.}=345$.

After removal of this substance, potassium cyanide, traces of ammonia, potassium benzoate, and *p*-tolualdehyde were identified in the solution.

Cinnamoylmandelonitrile and *Carbethoxymandelonitrile*.—Both these compounds gave benzoin, but from compounds derived from anisaldehyde no anisoin could be isolated from the products of the reaction with potassium hydroxide.

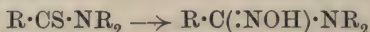
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LXXII.—*Amido-oximes and Thioamides.*

By WILLIAM FRASER RUSSELL.

DURING the investigation of α' -oximino- β -vinylquinclidine, a disintegration product of the cinchona alkaloids (Rabe, *Ber.*, 1908, 41, 68; W. F. Russell, *Diss.*, Jena, 1910), I was led to prepare some simpler amido-oximes with the view of comparing their behaviour with that of the above compound, and of determining whether they reacted easily with nitrous acid, giving the corresponding amides.

The disubstituted amido-oximes are best obtained either by Tiemann's method (*Ber.*, 1886, **19**, 1668), by the action of hydroxylamine on thioamides:



or by Werner's method (Werner and Buss, *Ber.*, 1894, **27**, 2197), by combining hydroximic chlorides with amines.

As will be seen from the experimental work, Tiemann's method appears to be suited only for thioamides of the formula $\text{R}\cdot\text{CS}\cdot\text{NHR}$, that is, for those containing a monosubstituted amido-group; these are easily converted into the corresponding oximes with evolution of hydrogen sulphide by boiling with hydroxylamine in alcoholic solution. The disubstituted thioamides of the formula $\text{R}\cdot\text{CS}\cdot\text{NR}_2$, on the other hand, are attacked only to a slight extent by hydroxylamine under the same conditions. The latter are best obtained by the interaction of hydroximic chlorides and suitable amines.

The thioamides were prepared in each case by the action of phosphorus pentasulphide on the corresponding amide.

EXPERIMENTAL.

Thioacetylpipeidine, $\text{CH}_3\cdot\text{CS}\cdot\text{NC}_5\text{H}_{10}$.

The reaction between phosphorus pentasulphide and acetylpipeidine takes place very easily. Two parts of acetylpipeidine were mixed with one part of finely powdered phosphorus pentasulphide in the cold, and the liquid mixture was thoroughly stirred. The reaction sets in at once, and much heat is produced. On cooling, the yellow mass was extracted with warm alcohol, and the filtered solution, on cooling, deposited the thioacetylpipeidine in small, yellow plates, which, on recrystallisation, were obtained quite colourless, and melted at 60—61°:

0.3540 gave 0.5780 BaSO_4 . $\text{S} = 22.42$.

$\text{C}_7\text{H}_{13}\text{NS}$ requires $\text{S} = 22.37$ per cent.

Action of Hydroxylamine on Thioacetylpipeidine.

1.4 Grams of thioacetylpipeidine (1 mol.) were dissolved in 40 c.c. of alcohol. Solutions of 1.38 grams of hydroxylamine hydrochloride (2 mols.) and 1.06 grams of anhydrous sodium carbonate (1 mol.) in a small amount of water were mixed and added, and the whole was boiled under a reflux condenser for six hours. At first, traces of hydrogen sulphide were evolved, and, later, ammonia from the decomposing hydroxylamine. From the product, 1 gram of thioacetylpipeidine was recovered unchanged, whilst only 0.2

gram of a substance, melting at 90—91°, could be isolated, which was identical with acetenylpiperidyloxime obtained by the action of piperidine on acetohydroximic chloride and described below.

Acetenylpiperidyloxime, $\text{CH}_3\cdot\text{C}(\text{:NOH})\cdot\text{NC}_5\text{H}_{10}$.

This was prepared by treating a solution of acetohydroximic chloride in ether with an ethereal solution of piperidine, and removing the piperidine hydrochloride formed. On evaporating the ethereal solution, an oil was obtained, which partly crystallised. The crystals were separated from the oily admixture by spreading on porous plate, and purified by recrystallisation from hot water. The substance melts at 91—92°, and is readily soluble in hot water or dilute acids:

0.1984 gave 34 c.c. N_2 at 12° and 740 mm. $\text{N}=20.04$.

$\text{C}_7\text{H}_{14}\text{ON}_2$ requires $\text{N}=19.7$ per cent.

The acetohydroximic chloride used in the above preparation was obtained by the action of chlorine on acetaldoxime by Piloty and Steinbock's method (*Ber.*, 1902, **35**, 3113). The results obtained by me differed from those of Piloty and Steinbock, in so far that the deep blue oily chloronitrosoethane produced on chlorinating the acetaldoxime did not spontaneously change into the colourless isomeric acetohydroximic chloride on keeping for a short time in ethereal solution. On evaporating the ethereal solution of the chloronitrosoethane, a partial transformation took place, and, from the green solution so obtained, the acetenylpiperidyloxime was prepared by carefully treating it with piperidine in ether. On account of this difficulty, the preparation could not be carried out quantitatively.

Action of Nitrous Acid on Acetenylpiperidyloxime.

1.5 Grams (1 mol.) of acetenylpiperidyloxime were treated in dilute sulphuric acid solution with a solution of 0.73 gram (1 mol.) of sodium nitrite in 10 c.c. of water at the ordinary temperature. A violent evolution of nitrous oxide took place, and, on extracting the solution with ether, 1.1 grams of acetyl piperidine were obtained, boiling at 224—226°:

0.2086 gave 20 c.c. N_2 at 12° and 740 mm. $\text{N}=11.3$.

$\text{C}_7\text{H}_{13}\text{ON}$ requires $\text{N}=11.2$ per cent.

Thiobenzoylpiperidine, $\text{C}_6\text{H}_5\cdot\text{CS}\cdot\text{NC}_5\text{H}_{10}$.

This compound was obtained by gently warming 20 grams of benzoylpiperidine with 10 grams of phosphorus pentasulphide. On cooling and extracting with warm alcohol, the thiobenzoylpiperidine

was obtained in deep yellow needles, which, on recrystallisation from alcohol, became pale yellow. The compound melts at 65—66°. The yield was about 13 grams:

0.5080 gave 0.5794 BaSO₄. S = 15.66.

C₁₂H₁₅NS requires S = 15.60 per cent.

Action of Hydroxylamine on Thiobenzoylpiperidine.

Ten grams of thiobenzoylpiperidine and 3.4 grams of hydroxylamine hydrochloride were boiled with a solution of 1.1 grams of sodium in 130 c.c. of alcohol* for forty-eight hours. Two grams of the thioamide were recovered, and 0.7 gram of benzenylpiperidyl-oxime (Found, N = 14.01. Calc., N = 13.72 per cent.) was obtained. The latter melted at 150°, and was identical with the product obtained by treating benzhydroximic chloride with piperidine (Ley and Krafft, *Ber.*, 1907, **40**, 704; these authors give the melting point as 136—137°).

Action of Nitrous Acid on Benzenylpiperidyl-oxime.

Like acetenylpiperidyl-oxime, this compound at once reacts with nitrous acid, with vigorous evolution of nitrous oxide, and benzoylpiperidine is formed. On treating 4 grams of the substance in dilute sulphuric acid with sodium nitrite solution, 2.7 grams of benzoylpiperidine, melting at 46—48°, were obtained.

Diphenylthiobenzamide, C₆H₅·CS·N(C₆H₅)₂.

This thioamide was prepared by Bernthsen (*Annalen*, 1878, **129**, 37) by treating benzenylisodiphenylamidine with hydrogen sulphide. By melting diphenylbenzamide (from benzoyl chloride and diphenylamine) with phosphorus pentasulphide, I obtained it as a deep yellow, crystalline compound, melting at 155° (Bernthsen gives 149—150°). From 2.7 grams of diphenylbenzamide, 1.5 grams of the thioamide were obtained.

Action of Hydroxylamine on Diphenylthiobenzamide.

1.5 Grams of diphenylthiobenzamide were boiled in alcoholic solution with hydroxylamine (2 mols.) for two days. From the solution were recovered 1.4 grams of the unchanged thioamide, and a minute quantity (about 0.1 gram) of a greyish-white substance was obtained on neutralising the acid extract. It was soluble in acids, and was probably benzenyldiphenylanilido-oxime.

* No action takes place if sodium carbonate is used as condensing agent.

Phenylethylthiobenzamide, $C_6H_5 \cdot CS \cdot NEtPh$.

Fifteen grams of phenylethylbenzamide, obtained from benzoyl chloride and ethylaniline, were treated with 8 grams of phosphorus pentasulphide in the usual manner. On extracting the product with alcohol, 13.5 grams of the thioamide were obtained. It crystallises from alcohol in pale yellow, feathery crystals, melting at 98° :

0.4008 gave 0.3884 $BaSO_4$. $S = 13.3$.

$C_{15}H_{15}NS$ requires $S = 13.27$ per cent.

Action of Hydroxylamine on Phenylethylthiobenzamide.

After 2.4 grams of phenylethylthiobenzamide had been boiled in alcoholic solution for two days with hydroxylamine, 2.3 grams were recovered unchanged, and traces of a grey substance, soluble in dilute acids, probably benzenylphenylethylanilido-oxime, were obtained.

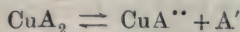
These experiments show how very resistant the disubstituted thioamides are towards hydroxylamine. On the other hand, Tiemann (*Ber.*, 1886, **19**, 1668) had prepared a number of monosubstituted thioamides, of which thiobenzanilide was one of the simplest, and found that they reacted readily with hydroxylamine. On repeating the preparation of benzenylanilido-oxime from thiobenzanilide, a good yield of the substance was obtained. It melts at $139-140^\circ$ (Müller, *Ber.*, 1889, **19**, 1669, gives 136°).

UNIVERSITY OF JENA.

LXXIII.—*The Colour and Ionisation of Cupric Salts.**

By NEVIL VINCENT SIDGWICK and HENRY THOMAS TIZARD.

IN a previous paper (*Trans.*, 1908, **93**, 188) we have shown that the colour of the cupric salts of weak acids, on dilution beyond the point where they cease to be green, diminishes without change of tint, approaching a limit which is different for each salt. We explained this by assuming the first dissociation:



to proceed nearly to completion before the second begins.

We are indebted to Dr. Ewan for kindly calling our attention to

* This paper corresponds with the abstract in *Proc.*, 1910, **26**, 67.

a paper of his on the same subject (*Proc. Roy. Soc.*, 1894, **57**, 117), which we had unfortunately overlooked. He measured by means of the spectrophotometer the colour of solutions of copper acetate much more dilute than ours ($N/200$ to $N/1400$). He showed that the colour of this salt was much deeper than that of the copper salts of strong acids, and that the difference diminished on dilution. These results agree with ours. Ewan also investigated the action of acid on the colour, and the relation of the colour to the conductivity. His conclusions on these points will be discussed later.

We have now re-examined with greater care the colour of the acetate, propionate, and formate, both in neutral and in acid solution. We have also measured the conductivity and viscosity of these solutions.

I.—Colour.

In our former paper we stated that the colour of these salts was not appreciably affected by hydrolysis. Further work has shown that this is not the case. The addition of acid to a solution of the acetate or propionate causes a considerable diminution of colour, which, however, practically reaches a limit when about one equivalent of acid has been added, further addition having no effect. Such a result cannot be due to the action of the acid on the dissociation of the salt or on the formation of complexes, for this would cause an increase of colour, and would continue on further addition of acid. It can only be due to the existence of a certain amount of hydrolysis in the original solution, which a moderate excess of acid is sufficient to destroy. This correction does not affect our general conclusions, since, as our numbers show, the colour-curve of the acidified solution is parallel to that of the neutral solution. In the case of the formate, excess of acid has practically no effect on the colour.

It is remarkable that Ewan finds (at a dilution of $N/200$ to $N/1400$) that the colour is increased by the presence of excess of acid. The differences, however, are only small (indeed, with one solution they are in the opposite direction), and it is possible that the effect may be reversed at these higher dilutions, although our results show no indications of such a tendency.

The methods of measurement were the same as in our previous work, but greater precautions were taken to secure accuracy. The solutions were analysed electrolytically both before and after they had been adjusted to the required strength. Each complete series of dilutions was examined in one day, the standard being compared with a $N/5$ -copper sulphate solution at the beginning and end of the measurements. Every value is the mean of at least four concordant readings taken by each of us. The whole series of

measurements for the neutral solutions were repeated after the lapse of some time, and, as will be seen, a satisfactory agreement was obtained. In the following tables an equivalent of acid means one molecule of acid to every molecule of copper salt; and the numbers give the values of what we previously called C_v : that is, the amount of colour of a gram-molecule of salt dissolved in V litres of water and contained in a tube of uniform diameter, the colour of a gram-molecule of copper sulphate dissolved in 5 litres of water contained in the same tube being taken as 1.

*Colour.**Copper Acetate.*

V .	Neutral.		Mean.	+ 1 equiv. + $3\frac{1}{2}$ equiv.		Diff.
	I.	II.		acid.	acid.	
5	6.91	6.93	6.92	6.16	—	0.76
7.5	6.34	6.32	6.33	5.56	5.55	0.77
8	—	—	(6.20) *	5.43	5.41	0.77
9	—	—	(5.98) *	5.21	5.19	0.77
10	5.81	5.77	5.79	5.01	4.99	0.78
12.5	5.51	5.53	5.52	4.74	4.76	0.78
15	5.35	5.30	5.33	4.52	—	0.81
20	5.01	5.00	5.01	4.19	—	0.82
25	4.81	4.75	4.78	3.97	—	0.81
30	4.53	4.50	4.52	3.75	—	0.77
35	4.38	4.38	4.38	3.63	—	0.75
45	4.21	4.18	4.20	3.42	—	0.78

* These values were obtained by interpolation from the curve.

Copper Propionate.

V .	Neutral.		Mean.	+ 1 equiv. acid.	+ 2 equiv. acid.	+ $2\frac{1}{2}$ equiv. acid.	Diff.
	I.	II.					
5	8.87	8.87	8.87	—	—	—	—
7.5	7.38	7.31	7.35	7.15	—	6.81	0.54
10	6.69	6.60	6.65	6.10	—	5.95	0.70
12.5	6.22	6.20	6.21	5.48	—	5.43	0.78
15	5.82	5.83	5.83	5.10	—	5.05	0.78
20	5.33	5.32	5.33	4.53	4.45	—	0.88
25	4.99	5.01	5.00	4.24	—	—	—
30	4.76	4.78	4.77	4.02	3.93	—	0.84
35	4.60	4.54	4.57	3.80	—	—	—
45	4.41	4.37	4.39	3.56	3.52	—	0.87

Copper Formate.

<i>V.</i>	Neutral.		Mean.	+ 2 equiv. acid.	Diff.
	I.	II.			
3	3·90	3·92	3·91	—	—
4·5	3·64	3·67	3·66	—	—
6	3·52	3·52	3·52	3·45	0·07
7·5	3·40	3·40	3·40	—	—
9	3·28	3·29	3·29	3·28	0·01
12	3·14	3·17	3·16	3·13	0·03
15	3·03	3·03	3·03	—	—
18	2·93	2·92	2·93	2·91	0·02
21	2·89	2·88	2·89	—	—
24	—	2·85	2·85	—	—
27	—	2·79	2·79	2·75	0·04

Ewan quotes measurements for *N*/267- and *N*/1400-copper acetate, and for *N*/7-copper sulphate. Taking our value 1·04 for the sulphate at this dilution, his numbers give (as the mean of the results for three different wave-lengths) for the colour of the acetate at *V*=267, 2·71, and at *V*=1400, 1·44.

The last column gives the difference in colour between the hydrolysed and the non-hydrolysed solutions. In the case of the acetate, the constancy of this difference is remarkable. Assuming that the colour of the hydrolytic product is independent of the dilution, and that its quantity is small (and its colour proportionately great), the amount of the hydrolysis must be the same throughout, as we should expect for the salt of a weak acid and a weak base, if the ionisation can be assumed to be complete. How far this conclusion is justified will be discussed later. With the propionate, the general results are the same. The diminution of colour is not complete on addition of one equivalent of propionic acid (a weaker acid than acetic), especially at higher concentrations of the salt; and the maximum difference of colour produced by the addition of acid is less here than at greater dilutions. But the stronger solutions still retain a distinct green tinge, which is increased by the presence of acid (and is no doubt due to the formation of complexes), so that the measurements obtained with them are not of great value. With the more dilute solutions the fall in colour becomes practically constant. In the case of the formate the differences (although in the same direction) are within the limits of experimental error. This may be due to the absence of hydrolysis with this stronger acid, or to the hydrolytic product having the same colour as the neutral salt, or to both causes. It will be shown later that the solution is probably hydrolysed to a small extent.

II.—Conductivity.

In order to throw further light on the question, we have measured the conductivity of these solutions. The electrolytic cell was of

the normal Ostwald pattern, but had the plates widely separated in order to increase the resistance. In place of the usual coil and telephone, a Fitzpatrick commutator was employed, with a galvanometer. Subsequent investigations by Mr. H. B. Hartley and Mr. T. S. Moore have shown that the resistances obtained by means of the commutator are not very trustworthy, and are affected by the speed at which it is run, but under the conditions of our experiments it is not probable that the errors due to this cause exceeded 0.3 per cent.

It is stated by Fousserreau (*Ann. Chim. Phys.*, 1887, [vi], 12, 553) that a dilute aqueous solution of copper acetate slowly diminishes in conductivity after it is made up. Thus he found that a $N/1057$ -solution increased nearly 3 per cent. in resistance after being kept for three days in the cold. On heating to 100° for an hour, the resistance was nearly doubled, but on cooling and allowing to remain, it gradually fell nearly to its original value. Other solutions (from $N/200$ to $N/1500$) gave similar results. He ascribes this to a slow process of hydrolysis.

We have repeated the work, and are quite unable to confirm it. The solution, if kept in a steamed-out Jena flask, does not alter perceptibly in a week. A neutral copper acetate solution (about $N/260$) was made up from the solid salt, and the resistance measured from time to time, with the following results:

Time after dissolving.	Resistance.
30 minutes	4208.0 ohms
40 "	4209.2 "
16 hours	4210.8 "
40 "	4211.0 "
7 days	4209.2 "

Thus the maximum variation was less than 0.1 per cent. If the liquid is heated (one hour at about 85°), the resistance certainly increases nearly 50 per cent., but this is due to the precipitation of copper oxide, which forms a black film on the surface of the glass. If the liquid is kept in contact with this film in the cold, it slowly redissolves it to a considerable extent, and the resistance falls again.

The conductivities of the three salts were determined (1) in neutral solution, (2) in presence of one equivalent, (3) in presence of two equivalents of the corresponding acid. The dilutions were made in the cell. This contained 30 c.c. of liquid, 10 c.c. of which were removed each time and replaced by 10 c.c. of water. The water used had a conductivity between 1 and 1.5×10^{-6} units. The measurements were in all cases repeated with new solutions, and they were checked by special dilutions made outside the cell.

The temperature, as in all the other measurements in this paper, was 18°.

Molecular Conductivity.

Dilution = <i>V</i> .	Acetate.			Propionate.		
	Neutral.	+1 equiv. acid.	+2 equiv. acid.	Neutral.	+1 equiv. acid.	+2 equiv. acid.
5.0	24.63	—	—	21.06	—	—
6.667	28.55	—	—	24.91	25.80	—
7.143	—	—	31.04	—	—	—
7.50	30.40	—	—	26.58	—	—
8.333	—	33.72	33.59	—	29.23	28.81
10.0	34.70	—	—	30.78	32.24	31.77
11.25	36.64	—	—	32.54	—	—
12.50	—	40.41	40.52	—	35.91	35.61
14.28	—	—	42.67	—	—	—
15.00	—	—	—	37.14	39.03	38.72
16.07	—	—	44.91	—	—	—
16.88	43.36	—	—	39.06	—	—
18.75	—	47.62	47.85	—	42.94	42.83
21.43	—	—	50.24	—	—	—
22.50	48.58	—	—	44.06	46.21	46.09
24.11	—	—	52.54	—	—	—
25.31	50.63	—	—	46.12	—	—
28.13	—	55.37	55.73	—	50.41	50.38
32.14	—	—	58.24	—	—	—
33.75	56.42	—	—	51.56	53.86	53.90
36.16	—	—	60.78	—	—	—
37.97	58.51	—	—	53.73	—	—
42.19	—	63.65	64.14	—	58.42	58.44
48.21	—	—	66.79	—	—	—
50.00	64.10	67.08	—	—	—	62.03
50.63	64.81	—	—	59.69	62.06	62.23
54.24	—	—	69.62	—	—	—
56.95	66.82	—	—	61.89	—	—
63.28	—	72.59	—	—	66.87	67.10
72.32	—	—	75.97	—	—	—
75.94	73.65	—	—	68.13	70.30	71.12
81.36	—	—	78.97	—	—	—
83.33	—	—	—	—	72.75	—
85.43	76.20	—	—	—	—	—
94.92	—	81.82	82.74	—	75.77	76.19
113.91	—	—	—	77.08	79.78	80.33
128.14	85.35	—	—	79.52	—	—
142.18	—	91.18	92.60	—	85.00	85.49
170.86	—	—	—	86.18	89.12	89.90
192.22	94.66	—	—	88.66	—	—
213.27	—	100.98	102.97	—	94.52	95.11
256.29	—	—	—	95.34	98.70	99.60
288.33	103.81	—	—	96.19	—	—

Molecular Conductivity.

<i>V</i> .	Formate.		
	Neutral.	+1 equiv. acid.	+2 equiv. acid.
3.0	31.33	—	—
4.0	36.55	38.00	—
4.5	38.65	—	—
5.0	—	42.34	43.27
6.0	44.34	46.16	46.97

Molecular Conductivity (continued).

<i>V.</i>	Formate.		
	Neutral.	+ 1 equiv. acid.	+ 2 equiv. acid.
6.75	46.65	—	—
7.5	—	50.82	51.82
9.0	—	54.84	55.96
10.13	55.25	—	—
11.25	—	59.85	61.18
13.50	61.67	64.24	65.72
16.88	—	69.51	71.30
20.25	71.38	74.34	75.90
22.78	74.28	—	—
25.31	—	79.84	82.10
30.00	81.09	—	86.67
30.38	81.30	84.92	87.17
34.17	84.32	—	—
37.97	—	90.91	93.54
45.56	91.69	96.20	99.22
51.26	94.76	—	—
56.95	—	102.43	105.88
68.34	102.14	107.87	111.99
75.00	104.47	—	114.04
76.89	105.49	—	—
85.43	—	114.57	119.16
102.52	—	119.98	125.61
128.14	—	126.93	132.81
153.77	—	132.32	140.16

The most remarkable point about these numbers is that at high concentrations the addition of a second equivalent of acid actually diminishes the conductivity both of the acetate and of the propionate. On dilution, this difference diminishes, and ultimately changes its sign, the two curves crossing in the case of the propionate, where the effect is most marked, at about $V=30$, and in that of the acetate at about $V=12$. This fall of conductivity cannot be due to a decrease in the ionic concentrations. The second equivalent must increase the number of ions (although only to a small extent with such weak acids), and especially must introduce more of the rapidly moving hydrogen ion, so that we should expect the conductivity to rise. The effect is increased by adding more acid, and is not confined to the salts of copper. The conductivity of a $N/10$ -copper acetate solution diminishes nearly 15 per cent. in the presence of 10 per cent. (17 equivalents) of acetic acid, and the same addition produces about the same result in a $N/20$ -solution of sodium acetate.* Since the conductivity falls without a diminution in the number of ions, the addition of acid must diminish the ionic velocity; and it is evident that it does so by increasing the viscosity of the solution.

The viscosities of these solutions were therefore measured.

* Similar results have been obtained by Rudolf (*Zeitsch. physikal. Chem.*, 1903, 43, 262).

III.—*Viscosity.*

We are indebted to Mr. Hartley for allowing us to carry out these measurements in the Balliol Laboratory, as well as for the loan of the necessary apparatus, and for much assistance in using it.

The viscometers were of the Ostwald pattern; two were employed, the time of flow for water being about three and six minutes respectively. The times were determined with a stop-watch reading to a fifth of a second. Every solution was measured in both tubes, and the determinations repeated if they did not agree. The solutions were made up with dust-free conductivity water. Both the densities and the viscosities are very nearly linear functions of the concentration, so that a comparatively small number of measurements is sufficient, the intermediate values being determined from the curve. As before, each salt was measured (1) in neutral solution, (2) in presence of one equivalent, (3) in presence of two equivalents of the corresponding acid. The temperature was 18°. The densities and viscosities are referred to those of water at 18° taken as unity.

Copper Acetate.

V.	Density.			Viscosity.		
	Neutral.	+ 1 equiv.	+ 2 equiv.	Neutral.	+ 1 equiv.	+ 2 equiv.
5	1·0216	1·0234	1·0252	1·1580	1·1887	1·2138
10	1·0109	1·0119	1·0128	1·0811	1·0971	1·1051
20	1·0056	1·0061	1·0069	1·0411	1·0500	1·0545
40	1·0024	1·0027	1·0034	[1·0205]	1·0250	1·0258
80	[1·0012]	1·0014	1·0017	—	1·0138	1·0147

Copper Propionate.

5	1·0208	1·0222	1·0235	1·2046	1·2505	1·2962
10	1·0107	1·0114	1·0121	1·1060	1·1260	1·1452
20	1·0054	1·0058	1·0061	1·0586	1·0659	1·0756
40	[1·0027]	[1·0029]	[1·0030]	1·0338	1·0366	1·0406
80	[1·0013]	[1·0014]	[1·0015]	[1·0202]	[1·0215]	1·0227

Copper Formate.

3	1·0380	1·0418	1·0455	1·1757	1·1880	1·2017
6	1·0193	1·0212	1·0231	1·0923	1·0948	1·0982
12	1·0097	1·0108	1·0118	1·0500	1·0513	1·0532
24	1·0051	[1·0056]	1·0060	1·0300	1·0302	1·0312
48	1·0027	[1·0029]	[1·0032]	1·0178	[1·0185]	1·0192

The values in brackets were obtained by interpolation.

The viscosity of acetic acid over this range of concentrations has since been measured at 25° (Rivett and Sidgwick, this vol., p. 732). Assuming its temperature-coefficient to be the same as that of water, we may compare the increase of viscosity which it produces in the

solution of the copper salt with that which it produces in water. In the following table, V gives the dilution of the copper salt (and hence that of one equivalent of acid), whilst the second column gives the increase of viscosity caused by the addition of the first equivalent of acid, the third column that caused by the second, and the fourth the difference between the viscosity of an aqueous solution of the acid alone at dilution V and that of water:

V .	1st equiv.	2nd equiv.	Acid alone.
5	0.0307	0.0251	0.0224
10	0.0160	0.0081	0.0112
20	0.0089	0.0045	0.0056

The large increase caused by the first addition of acid is obviously connected with the disappearance of hydrolysis.

IV.—*Discussion of Results.*

The most probable view as to the influence of viscosity on ionic velocity is that the latter is inversely proportional to the former, at any rate as a first approximation when the change in viscosity is not too great. Hence, in order to eliminate the influence of viscosity, the observed values of the molecular conductivity must be multiplied by those of the viscosity at the same concentrations.

For this purpose the values of μ were plotted against the cube root of the dilution, and from the smooth curves drawn through these points a series of values were interpolated for the dilutions at which the colour had been measured. The viscosity values were obtained in the same way. The results are given in the following tables. It will be seen that the correction brings the conductivities of the solutions with two equivalents of acid in all cases above those with one.

The subscripts 0, 1, and 2 refer to the three solutions (neutral, with one equivalent, with two equivalents of acid). The difference between the corrected conductivities with one and with two equivalents of acid is due to the greater concentration of the hydrogen ion (with its high velocity) in the second case, the change in the quantities of the other ions being so small that its effect on the conductivity may be neglected. Now, using the ordinary symbols, we have:

$$\begin{aligned} K \times C_{HA} &= C_{H^+} \times C_A, \\ \text{hence } \frac{C_{H^+}}{C_{HA}} &= \frac{K}{C_A}. \end{aligned}$$

As the concentration of the acetate ion is practically unaltered, the degree of dissociation of the acid will be the same (at any given value of V) whether one or two equivalents are present. Hence the amount of hydrogen ion present is proportional to the amount

Copper Acetate.

T.	Conductivity.			Viscosity.			$\mu_3\eta_1$.	$\mu_2\eta_2$.	$\delta = \mu_2\eta_2 - \mu_1\eta_1$.	M = $\mu_1\eta_1 - \delta$.	H.
	μ_0 .	μ_1 .	μ_2 .	η_0 .	η_1 .	η_2 .					
7.5	24.62	25.92	25.60	1.1580	1.1887	1.2138	30.81	31.07	0.26	30.55	2.04
8	30.37	32.08	31.88	1.1073	1.1280	1.1430	36.19	36.44	0.25	35.94	2.81
9	31.33	33.10	32.90	1.1009	1.1204	1.1340	37.09	37.31	0.22	36.87	2.38
10	33.11	35.00	34.81	1.0900	1.1079	1.1191	38.78	38.96	0.18	38.60	2.51
12.5	34.72	36.71	36.62	1.0811	1.0971	1.1051	40.27	40.47	0.20	40.07	2.53
15	38.38	40.40	40.45	1.0653	1.0784	1.0858	43.57	43.92	0.35	43.22	2.33
20	41.42	43.63	43.67	1.0547	1.0657	1.0714	46.49	46.79	0.30	46.19	2.50
25	46.46	48.88	49.00	1.0411	1.0500	1.0541	51.32	51.65	0.33	50.99	2.62
30	50.53	53.11	53.53	1.0331	1.0400	1.0430	55.23	55.83	0.50	54.73	2.53
35	54.02	56.64	56.98	1.0277	1.0334	1.0357	58.53	59.01	0.48	58.05	2.53
45	57.10	59.75	60.20	1.0237	1.0286	1.0308	61.46	62.05	0.59	60.87	2.41
60	62.20	65.01	65.51	1.0186	1.0222	1.0240	66.45	67.08	0.63	65.82	2.47
80	68.27	71.32	71.90	1.0141	1.0167	1.0180	72.51	73.19	0.68	71.83	2.60
100	74.52	77.74	78.53	1.0106	1.0125	1.0137	78.72	79.60	0.88	77.84	2.53
150	79.56	82.90	83.93	1.0084	1.0100	1.0109	83.73	84.84	1.11	82.62	2.38
200	88.92	92.48	94.01	1.0055	1.0067	1.0072	93.10	94.68	1.58	91.52	2.10
	95.50	99.28	101.43	1.0051	1.0050	1.0050	99.78	101.93	2.15	97.63	1.75

Copper Propionate.

Viscosity.

Conductivity.

V .	μ_0	μ_1	μ_2	η_0	η_1	η_2	$\mu_0\eta_0$	$\mu_1\eta_1$	$\mu_2\eta_2$	$\delta = \mu_2\eta_2 - \mu_1\eta_1$	$M = \mu_1\eta_1 - \delta$	H.
5	21.10	21.41	21.04	1.2046	1.2505	1.2962	25.31	26.77	27.27	0.50	26.27	0.96
7.5	26.52	27.52	27.16	1.1373	1.1661	1.1938	30.16	32.09	32.43	0.34	31.75	1.59
8	27.49	28.54	28.17	1.1294	1.1559	1.1814	31.05	32.99	33.28	0.29	32.70	1.65
9	29.22	30.41	30.05	1.1160	1.1391	1.1612	32.61	34.64	34.89	0.25	34.39	1.78
10	30.78	32.12	31.80	1.1060	1.1260	1.1452	34.04	36.17	36.42	0.25	35.92	1.88
12.5	34.30	35.88	35.60	1.0867	1.1017	1.1169	37.27	39.53	39.76	0.23	39.30	2.03
15	37.24	39.03	38.70	1.0741	1.0857	1.0982	40.00	42.37	42.51	0.14	42.23	2.23
20	42.34	44.20	43.96	1.0586	1.0659	1.0756	44.82	47.11	47.28	0.17	46.94	2.12
25	46.09	48.35	48.20	1.0487	1.0545	1.0615	48.33	50.98	51.16	0.18	50.80	2.47
30	49.37	51.76	51.73	1.0420	1.0469	1.0522	51.45	54.19	54.43	0.24	53.95	2.50
35	52.30	54.75	54.77	1.0372	1.0412	1.0458	54.25	57.00	57.28	0.28	56.72	2.47
45	57.12	59.72	59.83	1.0310	1.0336	1.0365	58.89	61.72	62.01	0.29	61.43	2.54
60	63.05	65.72	65.92	1.0251	1.0268	1.0284	64.63	67.58	67.79	0.31	67.17	2.54
80	69.17	72.01	72.34	1.0202	1.0215	1.0227	70.56	73.55	73.98	0.43	73.12	2.56
100	74.08	77.03	77.38	1.0168	1.0177	1.0181	75.32	78.39	78.77	0.38	78.01	2.69
150	83.08	86.17	86.67	1.0120	1.0125	1.0128	84.07	87.24	87.78	0.54	86.70	2.63
200	89.79	92.96	93.55	1.0093	1.0099	1.0103	90.62	93.88	94.51	0.63	93.25	2.63

Copper Formate.

3	31.32	32.0	33.17	1.1757	1.1887	1.2017	36.82	38.63	39.86	1.23	37.40	0.58
4.5	33.67	40.34	41.24	1.1202	1.1254	1.1310	43.32	45.40	46.65	1.25	44.15	0.83
6	43.66	45.68	46.82	1.0923	1.0953	1.0982	47.69	50.05	51.42	1.37	48.68	0.99
7.5	48.74	50.93	51.99	1.0757	1.0773	1.0799	52.43	54.87	56.14	1.27	53.60	1.17
9	52.68	54.94	56.02	1.0645	1.0656	1.0678	56.07	58.54	59.82	1.28	57.26	1.19
12	59.02	61.48	62.80	1.0503	1.0516	1.0532	62.00	64.65	66.14	1.49	63.16	1.16
15	64.22	66.82	68.23	1.0425	1.0430	1.0444	66.95	69.70	71.26	1.56	68.14	1.19
18	67.97	70.78	72.28	1.0371	1.0374	1.0385	70.49	73.43	75.07	1.64	71.79	1.30
21	72.27	75.24	76.95	1.0312	1.0317	1.0326	74.52	77.62	79.46	1.84	75.78	1.26
24	75.60	78.70	80.56	1.0297	1.0302	1.0311	77.84	81.07	83.07	2.00	79.07	1.23
27	78.53	81.78	83.86	1.0270	1.0277	1.0286	80.64	84.04	86.26	2.22	81.82	1.18
35	84.90	88.62	91.27	1.0217	1.0230	1.0237	86.74	90.06	93.42	2.76	87.90	1.16
50	94.00	98.58	101.92	1.0157	1.0174	1.0182	95.46	100.29	103.75	3.46	96.83	1.37
64	100.47	105.78	109.60	1.0120	1.0139	1.0146	101.68	107.27	111.20	3.93	103.34	1.66
80	106.42	112.48	116.92	1.0099	1.0118	1.0124	107.47	113.82	118.37	4.55	109.27	1.80
100	112.58	119.37	124.53	1.0080	1.0097	1.0102	113.47	120.54	125.80	5.26	115.28	1.81

of acetic acid, that is, is twice as great in the second solution as in the first. The conductivity due to this amount of hydrogen ion is given by the difference between $\mu_2\eta_2$ and $\mu_1\eta_1$ (column δ in the table). With the propionate, the value of δ shows a slight fall (less than 1 per cent. of the total, if we exclude the first value, obtained by extrapolation) down to $V=15$. This is probably caused in part by there still being some hydrolysis, as is also indicated by the colour. With the acetate, the same effect occurs to a much smaller extent, scarcely beyond the limits of experimental error. The same may be seen in the formate, in a still smaller degree. It is conceivable that the viscosity correction which we have applied is too large, and that the real factor is some fractional power of the viscosity. This would account for the small values of δ obtained with the most concentrated, and therefore the most viscous, solutions. At higher dilutions the value of δ steadily increases, as we should expect, with the increasing ionisation of the acid; and it is, of course, much larger with the much stronger formic acid.

By subtracting δ from $\mu_1\eta_1$ we get M , the true corrected value of the conductivity of the neutral solution of the salt in the absence of hydrolysis. This is given in the last column but one. It is to be noticed that any error in the measurement of $\mu_1\eta_1$ causes twice as large an error in M .

The last column (H) gives the difference between this final value and the observed value for the neutral, partly hydrolysed solution ($\mu_0\eta_0$). This difference corresponds with the degree of hydrolysis. In the acetate it remains practically constant up to $V=160$; in the propionate the same is the case for dilutions greater than $V=12.5$. In the formate (where its value is less certain owing to the magnitude of the correction δ), it is also constant except at the highest concentrations. The value of H for the acetate and propionate is about the same.

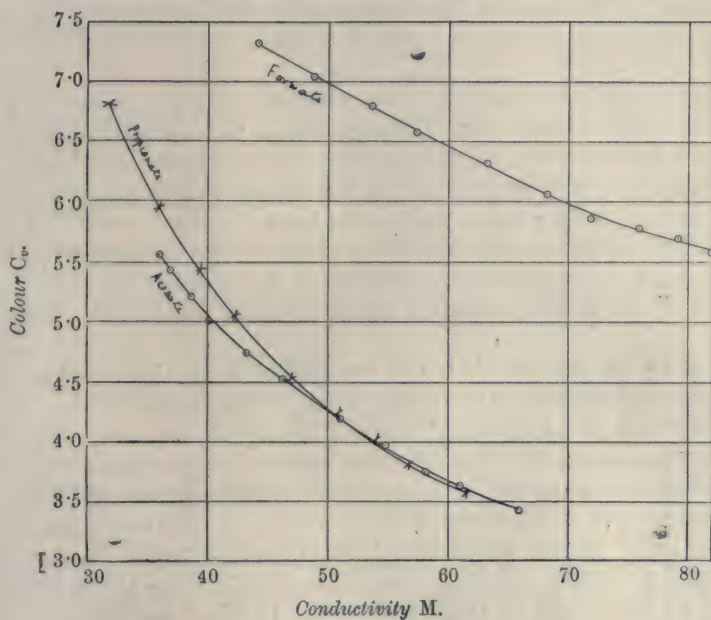
These results agree with the colour measurements, the change produced by hydrolysis being in both independent of the dilution. This is somewhat surprising. We should expect the difference in conductivity to increase with dilution, even if the hydrolysis did not, since the total conductivity increases. Our results thus seem to show that the hydrolysis diminishes with dilution, which is, to say the least, improbable. A rough estimate of the degree of hydrolysis can be arrived at in this way. The hydrolytic product may be taken to be undissociated. Now, with the acetate at $V=10$, the effect of destroying hydrolysis is to increase the conductivity by about 6 per cent. We may therefore assume that the solution is about 6 per cent. hydrolysed. We have already shown that the

removal of this amount of hydrolysis by the addition of acid diminishes the colour by about 0.8 unit. Hence the molecular colour of the basic acetate should be about 18—between three and four times that of the neutral salt.

If we assume (1) that over the range for which the colour was measured, only the first dissociation ($\text{CuA}_2 \rightleftharpoons \text{CuA}' + \text{A}'$) takes place, and (2) that the colour of CuA_2 and of CuA' is independent of the dilution, then the total value of the colour (hydrolysis being eliminated) is:

$$\begin{aligned} C_v &= a(1 - x) + bx \\ &= a + x(b - a), \end{aligned}$$

where a is the colour of CuA_2 , b that of CuA' , and x is the degree of ionisation. If we assume (3) that the ionic velocity is proportional



The values of C_v for the formate are multiplied by 2.

to the fluidity, and is not affected in any other way by the concentration, then the corrected conductivity of the solution is:

$$M = x \times \mu_{\infty},$$

where μ_{∞} is the molecular conductivity at infinite dilution of $\text{CuA}' + \text{A}'$. Hence, if we plot the values of the colour against those of the conductivity at various dilutions, we ought to get a straight line, independent of any particular law of dissociation. As the curves in the figure show, this is by no means the case. It follows

that either one of the assumptions (1) and (2) as to the colour, or the assumption (3) as to the conductivity, is false. Where the error lies we cannot at present say. As regards the possibility of hydration, either of the undissociated molecules or of the ions, it may be pointed out that this will not affect the results unless the proportion between the hydrated and unhydrated molecules, or between the various hydrates, changes with the dilution. Now, from the law of mass-action, if

$$\begin{aligned} \text{CuA}_2 + n\text{H}_2\text{O} &= \text{CuA}_{2,n}\text{H}_2\text{O}, \\ \text{then } \frac{C_{\text{CuA}_{2,n}\text{H}_2\text{O}}}{C_{\text{CuA}_2}} &= C_{\text{H}_2\text{O}}^n \times \text{Const.} \end{aligned}$$

Now, $C_{\text{H}_2\text{O}}$ is the weight of water in a litre of solution, and its value only varies from 986 for $N/5$ -acetate to 1000 at infinite dilution. Hence, unless the value of n is very large, the change in the proportion of the hydrates will be too small to produce a measurable result.

A possible disturbing cause is a combination of the excess of acid with the salt, as has been shown by one of us to occur with many organic acids (Proc., 1910, **26**, 60). This, however, can scarcely affect the colour, as no further fall was observed after one equivalent of acid had been added; and, as regards the conductivity, if the amount of combination is small, its effect will be eliminated by the method of calculation employed, since the second equivalent of acid will cause approximately twice as much combination as the first.

It is to be noticed that the conductivity of these salts rises steadily and largely on dilution, which suggests that in the more concentrated solutions they are not highly dissociated. Now, it would be possible from the corrected values of the conductivity (M) to calculate the degree of dissociation if we knew the velocity of the ion CuA' . This, however, is unknown, and cannot be directly determined. But if we assume that Ostwald's law holds for the salt, and that only the first dissociation ($\text{CuA}_2 \rightleftharpoons \text{CuA}' + \text{A}'$) takes place, we can arrive at this value by an indirect method. In the equation:

$$KV = \frac{\mu_v^2}{\mu_\infty (\mu_\infty - \mu_v)}$$

we can determine μ_v , that is, M , for any value of V , and hence there remain only two unknowns, K and μ_∞ . It is thus possible from every pair of measurements of the conductivity to calculate both the dissociation constant and the ionic velocity. We have calculated μ_∞ in this way for every successive pair of readings. This, of course, involves a much larger experimental error than if a pair of readings at some distance from one another (for example,

1st and 6th, 2nd and 7th, etc.) had been used; but it is more likely to show if at any point the nature of the process changes, either from a new law of dissociation coming in, or from the effect of the second dissociation making itself felt. A series of values of μ_{∞} is obtained in this way, which, as the table shows, although they vary very widely, have no definite tendency either upwards or downwards until a considerable dilution is reached.* The mean of these values was then taken, and from it the dissociation constant and the degree of ionisation were calculated for each dilution. If the assumptions are justified, concordant values of K should be obtained.

V.	Acetate.				Propionate.			
	M.	μ_{∞} .	α .	K.	M.	μ_{∞} .	α .	K.
5	30.55	100.2	0.301	0.0258	26.27	235.9]	0.239	0.0150]
7.5	35.94	104.9	0.354	0.0258	31.75	204.0]	0.289	0.0157]
8	36.87	104.1	0.363	0.0258	32.70	133.5]	0.298	0.0158]
9	38.60	87.7	0.380	0.0259	34.39	118.0]	0.313	0.0158]
10	40.07	85.5	0.394	0.0257	35.92	116.1	0.327	0.0159]
12.5	43.22	104.8	0.425	0.0252	39.30	111.6	0.358	0.0159]
15	46.19	102.0	0.455	0.0253	42.23	106.5	0.384	0.0160]
20	50.99	98.7	0.502	0.0253	46.94	108.1	0.427	0.0159]
25	54.73	107.7	0.539	0.0252	50.80	103.2	0.462	0.0159]
30	58.05	107.2	0.571	0.0254	53.95	106.2	0.491	0.0158]
35	60.87	115.4	0.599	0.0256	56.72	110.6	0.516	0.0157]
45	65.82	122.1]	0.648	0.0265]	61.43	117.1	0.559	0.0158]
60	71.83	—	—	0.0284]	67.17	120.6]	0.611	0.0160]
80	77.84	—	—	0.0314]	73.13	127.8]	0.665	0.0165]
100	—	—	—	—	78.01	127.1]	0.710	0.0174]
150	—	—	—	—	86.70	136.2]	0.789	0.0197]
200	—	—	—	—	93.25	—	0.849	0.0238]

Mean value of $\mu_{\infty} = 101.6$

Mean 109.9

Formate.

V.	M.	μ_{∞} .	α .	K.
3	37.40	131.8	0.272	0.0339
4.5	44.15	95.7	0.321	0.0337
6	48.68	211.9	0.354	0.0323
7.5	53.60	127.6	0.390	0.0332
9	57.26	123.9	0.416	0.0330
12	63.16	136.4	0.459	0.0325
15	68.14	95.7	0.496	0.0325
18	71.79	160.8	0.522	0.0317
21	75.78	144.9	0.551	0.0322
24	79.07	136.6	0.575	0.0324
27	81.82	—	0.595	0.0324
35	87.90	—	0.639	0.0324
50	96.83	—	0.704	0.0335
64	103.34	—	0.752	0.0355]
80	109.27	—	0.795	0.0384]
100	115.28	—	0.838	0.0439]

Mean 137.5

* The exceptionally high values given by the strongest solutions of the propionate are no doubt due to these solutions being (as we have already seen), to some extent hydrolysed.

The agreement in K is, as will be seen, very satisfactory on the whole. At the same time we do not feel great confidence in this line of argument, because the ionic velocities are so unexpectedly high. The following table gives the values for the CuA' ion, obtained by subtracting that of the A' ion from μ_{∞} ; and also a comparison of the mean K for the salt with that for the corresponding acid:

	Acetate.	Propionate.	Formate.
Velocity of $\text{CuA}' + \text{A}'$	101·6	109·9	137·5
„ A'	41·0	37·6	54·8
„ CuA'	60·6	73·2	82·7
Mean K for salt $\times 10^3$	25·5	15·9	32·7
K for acid $\times 10^3$	0·0180	0·0134	0·214

The low degree of dissociation, the formate, for example, appearing to be only half dissociated in $N/15$ -solution, is also an objection. It is commonly assumed that a salt of a weak acid and a weak base is highly ionised at moderate dilutions; and although the evidence for this assumption is somewhat scanty, recent work seems to show that it is justified, and that such a salt as ammonium acetate (see Lundén, *J. Chim. phys.*, 1907, **5**, 145; Noyes, Kato, and Sosman, *J. Amer. Chem. Soc.*, 1910, **32**, 159) is almost as highly dissociated as potassium chloride, more than 80 per cent. being ionised at $V=20$.

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LXXIV.—*The Condensation of Anisaldehyde with Resorcinol.*

By FRANK GEORGE POPE and HUBERT HOWARD.

SOME short time ago (this vol., p. 78) we described the condensation products obtained from benzaldehyde and resorcinol, and showed that in the presence of alkali hydroxides the course of the reaction followed that shown by Manasse (*Ber.*, 1894, **27**, 2409) to take place with phenols and formaldehyde. In the present communication we have carried out the same series of reactions, using anisaldehyde in place of benzaldehyde. The reaction is rather slower in this case if the reacting substances are kept at the ordinary temperature, the anisaldehyde being perceptible even after several days; but if the aldehyde and resorcinol are heated with the solution of the alkaline hydroxide in a closed vessel at $80\text{--}100^\circ$ for four hours, the reaction is practically complete.

EXPERIMENTAL.

2: 4-Dihydroxy-4'-methoxybenzhydrol,
 $C_6H_3(OH)_2 \cdot CH(OH) \cdot C_6H_4 \cdot OMe.$

13.6 Grams of anisaldehyde were heated with a solution of 11 grams of resorcinol in 250 c.c. of water containing 25 grams of sodium hydroxide, in a closed vessel in a water-bath for four hours. The blood-red solution so obtained was then diluted with about its own volume of water and acidified with dilute hydrochloric acid, when a very pale yellow precipitate of the hydrol was obtained. The precipitate was collected, washed with water, and dried. For analysis it was dissolved in boiling amyl acetate and the clear solution filtered into light petroleum, the precipitate being collected and dried:

0.1140 gave 0.2842 CO_2 and 0.0588 H_2O . $C=67.99$; $H=5.73$.

$C_{14}H_{14}O_4$ requires $C=68.29$; $H=5.69$ per cent.

2: 4-Dihydroxy-4'-methoxybenzhydrol, when freshly prepared, is a faintly yellow-coloured solid, which darkens rapidly on exposure to air. It does not melt on heating. It is soluble in glacial acetic acid, pyridine, or amyl acetate, but is insoluble in light petroleum. It is readily soluble in aqueous potassium hydroxide, and the solution, on concentration, yields a reddish-brown *dipotassium* salt, which crystallises from dilute alcohol in small needles:

0.4690 gave 0.2548 K_2SO_4 . $K=24.35$.

$C_{14}H_{12}O_4K_2$ requires $K=24.22$ per cent.

The *diacetyl* derivative was prepared by heating 5 grams of the hydrol with 25 grams of acetic anhydride and 1 gram of zinc dust for three hours under reflux. The solution was filtered from excess of zinc dust and poured into dilute alcohol, and the whole then warmed for some time on the water-bath in order to remove excess of acetic anhydride. The solid product was collected, washed, and crystallised from dilute acetic acid, from which it separated in small, almost colourless needles, which begin to decompose when heated to 120° :

0.1104 gave 0.2643 CO_2 and 0.0556 H_2O . $C=65.29$; $H=5.59$.

$C_{18}H_{18}O_6$ requires $C=65.45$; $H=5.45$ per cent.

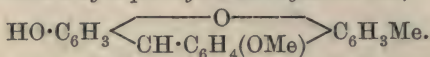
The *dibenzoyl* derivative was obtained by dissolving 4.92 grams of the hydrol in the calculated amount of sodium hydroxide (2 mols.) dissolved in 40 c.c. of water, and adding 5.62 grams of benzoyl chloride. The mixture was well shaken, the faintly yellow precipitate collected, washed, and crystallised from dilute acetic acid:

0.1170 gave 0.3190 CO_2 and 0.0534 H_2O . $C=74.36$; $H=5.07$.

$C_{28}H_{22}O_6$ requires $C=74.01$; $H=4.84$ per cent.

It begins to decompose at about 90°.

6-Hydroxy-4'-methoxy-9-phenyl-2-methylxanthen,



—2.46 Grams of the hydrol were mixed with 1.08 grams of *p*-cresol and 1 gram of anhydrous zinc chloride, and the mixture was heated at 160° for four hours. The product was extracted several times with water, and then redissolved in aqueous sodium hydroxide in the presence of a small quantity of zinc dust, the solution filtered, and the xanthen, precipitated by acetic acid, was washed and dried. For analysis, it was dissolved in chloroform, and the solution filtered into light petroleum, when a flocculent precipitate separated, which rapidly darkened on exposure, probably owing to slight oxidation and consequent formation of the corresponding fluorone derivative in slight amount. It melts at 112°:

0.1280 gave 0.3716 CO₂ and 0.0668 H₂O. C = 79.17; H = 5.80.

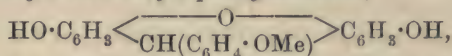
C₂₁H₁₈O₃ requires C = 79.24; H = 5.66 per cent.

The *acetyl* derivative was obtained by heating 2 grams of the xanthen with 2 grams of fused sodium acetate, 10 grams of acetic anhydride, and 1 gram of zinc dust for two to three hours under reflux. The product was poured into dilute alcohol, and warmed on the water-bath for some time to remove excess of acetic anhydride. On cooling, the solid mass was collected, washed, and then recrystallised from dilute acetic acid. It melts and decomposes at about 130—135°:

0.1084 gave 0.3042 CO₂ and 0.0550 H₂O. C = 76.54; H = 5.64.

C₂₃H₂₀O₄ requires C = 76.66; H = 5.55 per cent.

3: 6-Dihydroxy-4'-methoxy-9-phenylxanthen,



was prepared in a similar manner by heating 2.46 grams of the hydrol with 1.1 grams of resorcinol at 160° for four hours. The product was extracted with hot water, and the residue recrystallised from dilute alcohol, from which it separates in small needles:

0.1080 gave 0.2966 CO₂ and 0.0504 H₂O. C = 74.9; H = 5.18.

C₂₀H₁₆O₄ requires C = 75.00; H = 5.00 per cent.

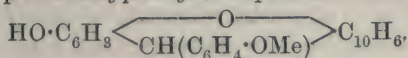
The *diacetyl* derivative was obtained by heating 2 grams of the xanthen with 2 grams of fused sodium acetate, 1 gram of zinc dust, and 10 grams of acetic anhydride for two hours. The product was poured into dilute alcohol, heated on the water-bath to remove excess of the anhydride, the solution cooled, and the precipitate collected and well washed with water. It was then dissolved in hot glacial acetic acid, water added until a faint turbidity was produced, a little zinc dust was also added, and the solution then filtered.

On cooling, the diacetate separated as a colourless, crystalline powder, which melted and decomposed at 140—150°:

0·1100 gave 0·2882 CO₂ and 0·0504 H₂O. C=71·45; H=5·09,

C₂₄H₂₀O₆ requires C=71·29; H=4·95 per cent.

8-Hydroxy-11-p-methoxyphenyl-β-naphthaxanthen,*



—2·46 Grams of the hydrol were mixed with 1·44 grams of β-naphthol and 1 gram of anhydrous zinc chloride, and the mixture heated at 160° for three hours. The product was extracted with water, dissolved in sodium hydroxide in the presence of a small quantity of zinc dust, and filtered. The xanthen was then precipitated from its alkaline solution by means of acetic acid, and the precipitate collected, washed, and dried. For analysis, it was dissolved in chloroform, and the clear solution then filtered into light petroleum, when it separated as a red-coloured, crystalline powder, which melted at 120°:

0·1048 gave 0·3120 CO₂ and 0·0482 H₂O. C=81·11; H=5·11.

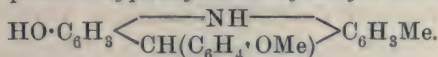
C₂₄H₁₈O₃ requires C=81·36; H=5·08 per cent.

The *acetyl* derivative was prepared in a similar manner to that used in the case of the other xanthen, and for analysis was dissolved in chloroform and precipitated by the addition of light petroleum. It was thus obtained as a brown-coloured powder, which melts at 95°:

0·1074 gave 0·3095 CO₂ and 0·0492 H₂O. C=78·59; H=5·01.

C₂₆H₂₀O₄ requires C=78·79; H=5·05 per cent.

8-Hydroxy-5-p-methoxyphenyl-3-methyldihydroacridine,



—This substance was prepared by heating 2·46 grams of the hydrol with 1·07 grams of *p*-toluidine for four hours at 160°. The product was extracted with water, collected and washed, and then dissolved in sodium hydroxide solution in the presence of a small quantity of zinc dust. The solution was filtered, and the dihydroacridine precipitated by the addition of acetic acid, collected, washed, and dried. For analysis, it was dissolved in benzene, and precipitated from the benzene solution by the addition of light petroleum. It separates as an almost colourless, microcrystalline powder, but soon becomes reddish-brown on exposure to air. It melts at 110°:

0·1180 gave 0·3442 CO₂ and 0·0654 H₂O. C=79·55; H=6·16.

0·1920 „ 7·6 c.c. N₂ (dry) at 17° and 750 mm. N=4·60.

C₂₁H₁₉O₂N requires C=79·49; H=5·99; N=4·41 per cent.

* Compare this vol., p. 82.

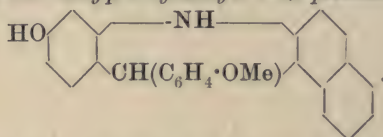
The *acetyl* derivative was prepared in the usual way by heating the hydroacridine with acetic anhydride and fused sodium acetate in the presence of zinc dust. The product was poured into dilute alcohol, and warmed to remove the excess of anhydride. It was then dissolved in glacial acetic acid, the solution poured into water, and the resulting precipitate collected, washed, and dried. For analysis it was dissolved in benzene and reprecipitated by the addition of light petroleum, when it separated in minute, almost colourless needles, decomposing at 140° :

0.1086 gave 0.3048 CO_2 and 0.0532 H_2O . $\text{C}=76.55$; $\text{H}=5.44$.

0.1860 „ 6.8 c.c. N_2 (dry) at 17° and 740 mm. $\text{N}=4.19$.

$\text{C}_{23}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=76.88$; $\text{H}=5.85$; $\text{N}=3.90$ per cent.

10-Hydroxy-7-p-methoxyphenyldihydro- $\alpha\beta$ -phenonaphthacridine,



—2.46 Grams of the hydrol were heated with 1.43 grams of β -naphthylamine for four hours at 160° . The product was extracted with water, dissolved in glacial acetic acid in the presence of a small quantity of zinc dust, filtered, and reprecipitated by the addition of water. It was collected, washed and dried, and then dissolved in benzene and reprecipitated by the addition of light petroleum, when it separates as a nearly colourless, crystalline powder, which darkens on exposure:

0.1120 gave 0.3360 CO_2 and 0.0570 H_2O . $\text{C}=81.82$; $\text{H}=5.65$.

0.2502 „ 8.8 c.c. N_2 (dry) at 13° and 743 mm. $\text{N}=4.1$.

$\text{C}_{24}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C}=81.87$; $\text{H}=5.38$; $\text{N}=3.97$ per cent.

The *acetyl* derivative was prepared in the usual manner, and crystallises from dilute acetic acid as an almost colourless powder, decomposing at 110° :

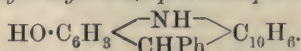
0.1038 gave 0.3000 CO_2 and 0.0516 H_2O . $\text{C}=78.82$; $\text{H}=5.52$.

0.2533 „ 8.4 c.c. N_2 (dry) at 20° and 746 mm. $\text{N}=3.79$.

$\text{C}_{26}\text{H}_{21}\text{O}_3\text{N}$ requires $\text{C}=78.99$; $\text{H}=5.31$; $\text{N}=3.54$ per cent.

As we had not prepared the corresponding dihydroacridine from 2:4-dihydroxybenzhydrol at the time of our last communication, we describe it here.

10-Hydroxy-7-phenyldihydro- $\alpha\beta$ -phenonaphthacridine,



—Three grams of 2:4-dihydroxybenzhydrol were heated with 2 grams of β -naphthylamine and 2 grams of anhydrous zinc chloride for four hours at 200° . The product was purified as in the case of

the compound just described, and purified for analysis by solution in chloroform and reprecipitation with light petroleum. It is obtained as a red, flocculent precipitate, which is easily soluble in benzene, chloroform, pyridine, or alcohol. It melts at 116° ;

0.1200 gave 0.3754 CO_2 and 0.0584 H_2O . $\text{C} = 85.32$; $\text{H} = 5.41$.

0.3840 „ 15.4 c.c. N_2 (dry) at 17° and 750 mm. $\text{N} = 4.66$.

$\text{C}_{23}\text{H}_{17}\text{ON}$ requires $\text{C} = 85.45$; $\text{H} = 5.26$; $\text{N} = 4.33$ per cent.

The *acetyl* derivative was prepared in the usual manner; it crystallises from alcohol as an almost colourless, microcrystalline powder, which decomposes when heated to 100° :

0.1000 gave 0.3010 CO_2 and 0.0472 H_2O . $\text{C} = 82.09$; $\text{H} = 5.24$.

0.2573 „ 8.6 c.c. N_2 (dry) at 12° and 743 mm. $\text{N} = 3.91$.

$\text{C}_{25}\text{H}_{19}\text{O}_2\text{N}$ requires $\text{C} = 82.19$; $\text{H} = 5.21$; $\text{N} = 3.84$ per cent.

The fact that the hydroxyxanthen and dihydroacridines mentioned above cannot be obtained colourless is, we think, due to the fact that oxidation of these substances takes place very rapidly, with consequent production of a certain amount of the corresponding fluorone and acridine derivatives, since we find that these fluorones and acridines are highly coloured substances.

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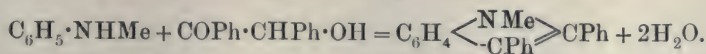
(UNIVERSITY OF LONDON).

LXXV.—*Preparation of Substituted Indoles from Benzoin and Secondary Arylamines.*

By MARION BROCK RICHARDS.

JAPP AND MURRAY (Trans., 1894, **65**, 889) showed that by heating benzoin with primary arylamines, in presence of zinc chloride or of the hydrochloride of the amine, 2:3-diphenylindoles could be prepared.

The author now finds that, by employing secondary in place of primary arylamines, analogous indoles may be obtained. Thus, by the interaction of benzoin and methylaniline, in presence of zinc chloride or of methylaniline hydrochloride, 2:3-diphenyl-1-methylindole is formed, according to the equation:



In like manner, by employing other secondary arylamines, other similar diphenylindoles have been prepared.

In the account of the experimental results, only that method of preparation is described which gave the best yield. In the case of the phenylnaphthylamine compounds, the yield by both methods was poor, but the product of the preparation in which the hydrochloride was used was much more easily purified. In this case, too, a variation in the method had to be introduced, the hydrochlorides of the phenylnaphthylamines being so unstable as to be decomposed by water. By conducting the experiment in an atmosphere of hydrogen chloride, the reaction was enabled to proceed by the momentary formation of the hydrochloride.

EXPERIMENTAL.



A mixture of 10.6 grams of benzoin, 16 grams of methylaniline, and 7.2 grams of methylaniline hydrochloride was heated to its boiling point until no more water was given off. The product was dissolved in benzene, and the solution, after being extracted with hydrochloric acid, was distilled under diminished pressure. The distillate, which passed over at about 280° , crystallised from glacial acetic acid in clusters of colourless needles (Found, $\text{C}=88.88$; $\text{H}=6.13$; $\text{N}=4.95$. Calc., $\text{C}=89.05$; $\text{H}=6.01$; $\text{N}=4.95$ per cent.), melting at 137° (Bischler and Fireman, *Ber.*, 1893, **26**, 1345, give 139°).

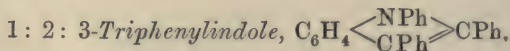


This was prepared by the same method as the preceding indole. The proportions employed were 10.6 grams of benzoin, 18 grams of ethylaniline, and 7.9 grams of ethylaniline hydrochloride. The product was treated in the same way. The distillate crystallised from alcohol in slender, colourless prisms, melting at 132.7° :

0.2046 gave 0.6679 CO_2 and 0.1188 H_2O . $\text{C}=89.03$; $\text{H}=6.45$.

0.2618 „ 10.8 c.c. N_2 (moist) at 16° and 752 mm. $\text{N}=4.76$.

$\text{C}_{22}\text{H}_{19}\text{N}$ requires $\text{C}=88.89$; $\text{H}=6.40$; $\text{N}=4.71$ per cent.

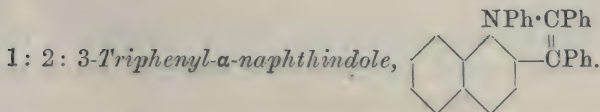


Twenty-one grams of benzoin, 25 grams of diphenylamine, and 30 grams of zinc chloride were heated until water ceased to be evolved, the product being treated exactly as in the previous cases. The distillate crystallised from glacial acetic acid in small, white, glistening laminæ, and from alcohol in voluminous masses of minute needles, melting at 186° :

0.2003 gave 0.6650 CO_2 and 0.1016 H_2O . $\text{C}=90.55$; $\text{H}=5.64$.

0.2408 „ 8.6 c.c. N_2 (moist) at 17° and 753.5 mm. $\text{N}=4.11$.

$\text{C}_{26}\text{H}_{19}\text{N}$ requires $\text{C}=90.43$; $\text{H}=5.51$; $\text{N}=4.06$ per cent.



21.2 Grams of benzoïn and 32.9 grams of phenyl- α -naphthylamine were heated in an oil-bath at 250° for about four hours in a continuous current of hydrogen chloride. The product was dissolved in glacial acetic acid, and the crystals which separated, after recrystallisation from acetic acid, gave very light, colourless needles, melting at 253° . Distillation of the mother liquor under diminished pressure yielded only benzoïn and phenyl- α -naphthylamine:

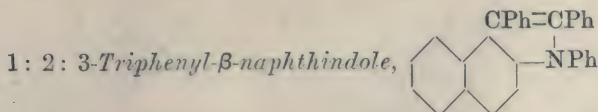
0.2082 gave 0.6938 CO_2 and 0.1006 H_2O . $\text{C}=90.88$; $\text{H}=5.37$.

0.3452 „ 10.5 c.c. N_2 (moist) at 17° and 743.7 mm. $\text{N}=3.46$.

$\text{C}_{30}\text{H}_{21}\text{N}$ requires $\text{C}=91.14$; $\text{H}=5.32$; $\text{N}=3.54$ per cent.

In the formation of this compound the condensation has been assumed to take place with the naphthyl rather than with the phenyl group, thus yielding a naphthindole instead of an indole. This is more in accordance with the greater mobility of the hydrogen atoms of naphthalene as compared with those of benzene.

As sodium does not act on an ethereal solution of 1 : 2-diphenyl- α -naphthindole, it was not possible to obtain the compound just described through the agency of bromobenzene.



This was prepared in the same way as triphenyl- α -naphthindole, the same weights of the corresponding substances being taken. The product, crystallised from acetic acid, yielded colourless needles, melting at 172.5° . On distilling the mother liquor under diminished pressure, a further quantity of substance was obtained from the distillate which passed over above the range of the thermometer (360°):

0.2038 gave 0.6802 CO_2 and 0.0981 H_2O . $\text{C}=91.03$; $\text{H}=5.35$.

0.3391 „ 10.7 c.c. N_2 (moist) at 18° and 764 mm. $\text{N}=3.66$.

$\text{C}_{30}\text{H}_{21}\text{N}$ requires $\text{C}=91.14$; $\text{H}=5.32$; $\text{N}=3.54$ per cent.

With regard to the constitution of this compound, the same assumption has been made as in the case of the foregoing triphenyl-

α -naphthindole. Moreover, it has been assumed that the compound is an $\alpha\beta$ -naphthalene derivative, the well-known difficulty of forming $\beta\beta$ -derivatives of naphthalene rendering the latter constitution improbable.

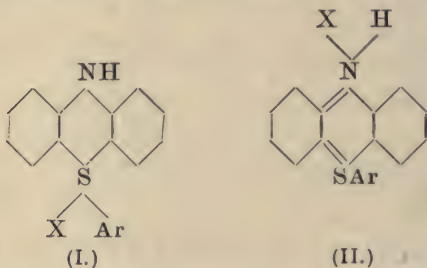
This research was suggested by Professor Japp and carried out under his supervision, and the author wishes to thank him for the interest he has always taken in the work.

CHEMICAL DEPARTMENT,
UNIVERSITY OF ABERDEEN.

LXXVI.—*Derivatives of S-Alkylphenazothionium.*

By EDWARD DE BARRY BARNETT and SAMUEL SMILES.

IN previous communications to the Society it has been shown that the properties of the sulphonium complex in derivatives of *S*-phenylphenazothionium vary according to the nature of the substituents in the thiodiphenylamine nucleus. It was also shown that the salts of these bases may assume either the true sulphonium form (I) or the quinonoid sulphonium structure (II). In the majority of sub-



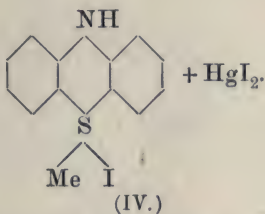
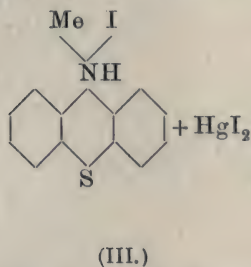
stances hitherto examined, the salts have been found to exist in the true sulphonium form; in fact, it is only in the case of the tetranitro-derivative that the quinonoid salt is obtained. The intramolecular conditions which determine the structure of these salts have not yet been elucidated, and it was with this object in view that the following experiments were performed. In all previous experiments made to determine these relations, the character of the thiodiphenylamine nucleus alone was varied, the third aryl group of the sulphonium complex being always phenetyl or hydroxyphenyl. We therefore desired to examine some derivatives of this group in which the third hydrocarbon nucleus is of an entirely different

character, and for this purpose we undertook the preparation of the alkyl derivatives.

The reactivity of aromatic sulphides with alkyl iodides is very sluggish; in fact, the direct union of these reagents is not easy to accomplish. The same inactivity may be observed with the bivalent sulphur group in thiodiphenylamine. Bernthsen (*Annalen*, 1885, **230**, 88) has shown that, although thiodiphenylamine does not react with methyl iodide at the ordinary temperature, it is merely converted into the *N*-methyl derivative when heated with that reagent to 100°, hydrogen iodide being liberated. We have frequently had occasion to repeat this experiment, but we have never been able to detect the sulphonium iodide in the product.

However, it has been elsewhere shown (Hilditch and Smiles, *Trans.*, 1907, **91**, 1393) that the addition of alkyl iodide to the aliphatic sulphides is enormously facilitated by the presence of mercuric iodide, and we find, on applying this reagent to thiodiphenylamine, that the sulphonium iodide is readily formed.

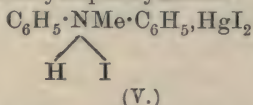
On general grounds, it is possible that the addition of alkyl halide to thiodiphenylamine may take place at the tervalent nitrogen (III) or at the bivalent sulphur (IV); but it may be



shown that the former alternative is incorrect. On inspecting the formula (III), it is evident that, according to this scheme, the product of the reaction must be regarded as the double salt of the hydriodide of *N*-methylthiodiphenylamine with mercuric iodide. If this were correct, it should be possible to synthesise the salt from these components, but all attempts to produce the substance in that manner have been unsuccessful. Again, from the fact that the hydriodide of *N*-methylthiodiphenylamine is not a stable salt, it must be expected that a double salt of this structure (III) would show similar instability, and when boiled with water would decompose, liberating hydrogen iodide. Moreover, when treated with alkali hydroxide or sodium sulphide, the substance should furnish *N*-methylthiodiphenylamine, and with the latter reagent hydrogen sulphide would be formed at the same time.

In order to verify these predictions of the behaviour of a sub-

stance containing this structure, we have prepared the corresponding derivative (V) of *N*-methyldiphenylamine:



This substance is readily decomposed by boiling water, yielding hydrogen iodide, and by sodium sulphide, giving hydrogen sulphide.

Turning to the compound the structure of which is in question, it is found that prolonged treatment with boiling water does not liberate even a trace of hydrogen iodide, and that sodium sulphide easily yields thiodiphenylamine and methyl sulphide. This behaviour is to be expected of the sulphonium double salt (IV), for it is evident that the sulphide of the base will first be formed, and, since the sulphides are generally less stable than most other sulphonium salts, decomposition would then proceed in the manner indicated. In this connexion reference may be made to an observation of Brown and Blaikie, who found (*J. pr. Chem.*, 1881, [ii], 23, 395) that the sulphide of trimethylsulphonium is resolved into methyl sulphide by warming the aqueous solution.

These facts show that the product of the action of methyl iodide on thiodiphenylamine in presence of mercuric iodide is the double salt of the sulphonium iodide, and it will be recalled that methyl iodide and thiodiphenylamine alone at 100° yield the *N*-methyl derivative. The selective action of the alkyl halide under the former set of conditions is clearly due to the influence of the mercuric iodide, which increases the reactivity of the bivalent sulphur. An experiment made with diphenylamine, mercuric iodide, and methyl iodide under the same conditions showed that the reactivity of the trivalent nitrogen is not appreciably increased by the presence of the inorganic iodide, since the formation of the required double salt was scarcely complete after four days, whilst with thiodiphenylamine the reaction is complete in about one hour.

The same reaction takes place with *N*-methylthiodiphenylamine, but much more slowly, and with much smaller yield. This confirms the previous observation made on oxidation of these derivatives: that the reactivity of the bivalent sulphur in *N*-methylthiodiphenylamine is less than in thiodiphenylamine. It is thus clear that some intimate relation exists between the trivalent nitrogen and the bivalent sulphur in these substances; but it cannot be expressed by the usual formulæ.

When the previously-mentioned sulphonium salts are treated with excess of silver oxide, the *S*-methylphenazothionium derivative is obtained; this substance is described in a later portion of this paper.

EXPERIMENTAL.

S-Methyldiphenylamine-o-sulphonium Iodide.

A saturated solution of 20 grams of thiodiphenylamine in acetone was mixed with 45 grams of mercuric iodide* and excess of methyl iodide. The mixture was set aside at the ordinary temperature and shaken at frequent intervals. The course of the reaction was indicated by the gradual dissolution of the mercuric iodide, which, after the lapse of about one and a-half hours, had completely disappeared, and was replaced by a crystalline precipitate of the required additive product. To ensure the complete precipitation of this substance, the mixture was not disturbed until a further two hours had elapsed, when the solid material was collected and washed with a little acetone. A further small quantity was obtained by allowing the filtrates to evaporate at the ordinary temperature. The total yield was almost theoretical.

S-Methyldiphenylamine-o-sulphonium iodide mercuri-iodide forms pale yellow prisms, which are sparingly soluble in cold acetone. When obtained from this medium, the substance retains one molecular proportion of the solvent. Thus, a sample which had been dried at the ordinary temperature gave the following numbers on analysis:

0.238 gave 0.194 CO_2 and 0.0467 H_2O . $\text{C} = 22.2$; $\text{H} = 2.2$.

0.1951 „ 0.160 CO_2 „ 0.0373 H_2O . $\text{C} = 22.3$; $\text{H} = 2.1$.

$\text{C}_{13}\text{H}_{12}\text{NIS}, \text{HgI}_2, (\text{CH}_3)_2\text{CO}$ requires $\text{C} = 22.5$; $\text{H} = 2.1$ per cent.

When heated at 100° , the crystals disintegrate, losing the acetone of crystallisation:

2.5682 lost 0.181 at 100° . Loss = 7.0.

$\text{C}_{13}\text{H}_{12}\text{NIS}, \text{HgI}_2, \text{C}_3\text{H}_6\text{O}$ requires $\text{C}_3\text{H}_6\text{O} = 6.80$ per cent.

When freed from acetone by this means, the substance was again analysed:

0.1798 gave 0.1292 CO_2 and 0.025 H_2O . $\text{C} = 19.6$; $\text{H} = 1.5$.

$\text{C}_{13}\text{H}_{12}\text{NIS}, \text{HgI}_2$ requires $\text{C} = 19.6$; $\text{H} = 1.5$ per cent.

This double salt melts and decomposes at 145° . It may be submitted to prolonged boiling with water without undergoing decomposition, but it is rapidly attacked by sodium sulphide in alcoholic solution.

Action of Sodium Sulphide.—The finely powdered substance was suspended in alcohol, in which excess of sodium sulphide had been dissolved. On warming the mixture, methyl sulphide was evolved,

* It may be remarked that thiodiphenylamine forms a double salt with mercuric iodide, but this was not isolated.

whilst mercuric sulphide was precipitated. When the decomposition was complete, the colourless liquid was separated from the mercuric sulphide by filtration, and then poured into water. The precipitate was collected and recrystallised from hot acetone. Analysis showed that the substance was thiodiphenylamine (Found, $C=71.7$; $H=4.9$. Calc., $C=72.3$; $H=4.6$ per cent.).

It melted at $180-181^\circ$ whether alone or mixed with a sample of thiodiphenylamine obtained from another source.

Several attempts were made to obtain the sulphonium iodide from the previously-described double salt by reduction with hydrazine in alkaline solution, when the mercury is precipitated in the finely divided state; but the product was amorphous, and did not invite further investigation. The action of silver oxide on this double salt is described in a subsequent paragraph.

N-Methyldiphenylamine hydriodide mercuri-iodide was obtained from diphenylamine, methyl iodide, and mercuric iodide under the same conditions as those described with thiodiphenylamine. The reaction is very much more sluggish than with thiodiphenylamine, since it was not complete until four days had elapsed. As the required double salt is very soluble in acetone, it was not precipitated during the reaction, and it was obtained by allowing the solution to evaporate at the ordinary temperature.

The double salt separates from acetone in transparent, yellow prisms, which melt at 145° :

0.2370 gave 0.1757 CO_2 . $C=20.2$.

$C_{13}H_{12}NI, HgI_2$ requires $C=20.2$ per cent.

When boiled with water it is at once decomposed, yielding hydriodic acid, and with sodium hydrosulphide it furnishes mercuric sulphide, hydrogen sulphide, and *N*-methyldiphenylamine.

N-S-Dimethyldiphenylamine-o-sulphonium Iodide.

A concentrated solution of *N*-methylthiodiphenylamine in cold acetone was mixed with an equimolecular proportion of mercuric iodide and excess of methyl iodide. The reaction was allowed to proceed at the ordinary temperature, the contents of the flask being shaken at intervals. After the lapse of about three days, an almost quantitative yield of the required double salt was precipitated. This was collected and recrystallised from boiling acetone, in which it was sparingly soluble:

0.1843 gave 0.1398 CO_2 and 0.0278 H_2O . $C=20.7$; $H=1.68$.

0.1718 „ 0.1300 CO_2 „ 0.0303 H_2O . $C=20.6$; $H=1.96$.

$C_{14}H_{14}NIS, HgI_2$ requires $C=20.76$; $H=1.73$ per cent.

N-S-Dimethyldiphenylamine-*o*-sulphonium iodide mercuri-iodide forms transparent, yellow prisms, which melt at 164°.

During the reaction by which this substance is produced, a double salt of mercuric iodide and *N*-methylthiodiphenylamine is formed as a preliminary product. This compound was obtained by warming a solution of *N*-methylthiodiphenylamine in acetone with excess of mercuric iodide, when a portion of the latter reagent dissolved. On cooling, *N*-methylthiodiphenylamine mercuri-iodide is precipitated in bright yellow leaflets:

0.2018 gave 0.2614 CO₂ and 0.0478 H₂O. C=35.32; H=2.63.

2C₉H₁₁NS, HgI₂ requires C=35.45; H=2.6 per cent.

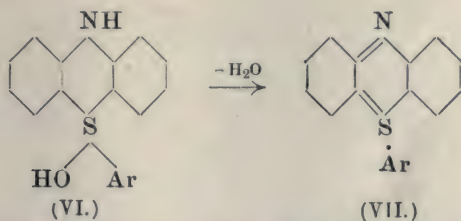
The substance readily decomposes into the components when heated, but when rapidly warmed it melts at 150—153°.

The previously-described sulphonium double salt is stable in presence of boiling water, but is readily decomposed by sodium sulphide.

Action of Sodium Sulphide.—The reaction was carried out under the same conditions as those already described with the similar derivative of thiodiphenylamine. Methyl sulphide was evolved and, when the reaction was complete, the filtered liquid was poured into water, and the precipitate which formed was recrystallised from alcohol. The substance melted at 100° when heated alone or mixed with a sample of *N*-methylthiodiphenylamine (Found, C=73.3; H=5.4. Calc., C=73.24; H=5.63 per cent.).

S-Methylphenazothionium.

It has been shown in a previous paper (Trans., 1908, **93**, 150) that the sulphonium hydroxides of *S*-phenylphenazothionium (VI), when liberated from the salts by means of alkali hydroxide, lose the elements of water, and are then transformed into the derivatives of *S*-phenylphenazothionium (VII):



It is therefore to be expected that the *S*-methyl derivative would be formed in a similar manner. Accordingly, the finely powdered double salt of *S*-methyldiphenylamine-*o*-sulphonium iodide (p. 983)

was treated with excess of silver oxide in warm alcohol. After the lapse of a few minutes the solution became dark red in colour, but the reaction was allowed to proceed for an hour and a-half, the mixture being vigorously shaken at frequent intervals. The mixture of silver and mercuric oxides was then collected, and the filtrates were evaporated in a vacuum. The residue consisted of a gummy, red mass, from which no crystalline product could be isolated, and it evidently consisted for the greater part of oxidation products. The basic constituents were removed by extraction with cold concentrated hydrochloric acid, which dissolved the required substance, forming a deep red solution of the hydrochloride. By diluting the acid solution, a small quantity of insoluble impurity was precipitated, and the remaining product was further purified by fractional precipitation with alkali hydroxide from acid solution. Finally, a solution of *S-methylphenazothionium hydrochloride* was obtained, and the salt was isolated for analysis by conversion into the platinichloride. The *platinichloride* forms reddish-brown needles of high melting point; it is insoluble in water or alcohol. After being dried at 100° , a sample gave the following numbers on analysis:

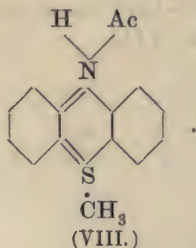
0.2656 gave 0.3680 CO_2 and 0.0778 H_2O . $\text{C}=37.78$; $\text{H}=3.25$.

0.2142 ,, 0.0488 Pt. $\text{Pt}=23.2$.

$(\text{C}_{13}\text{H}_{12}\text{NClS})_2\text{PtCl}_4$ requires $\text{C}=37.35$; $\text{H}=2.87$; $\text{Pt}=23.3$ per cent.

The yield of the hydrochloride was very small.

On treating the hydrochloride with alkali hydroxide or carbonate, the base is liberated as a red, unstable oil, but attempts to obtain this in the crystalline state were unsuccessful. All salts of this base which have been prepared are red in colour, and from this fact and from analogy to the *S*-aryl derivatives, it seems that they are not the true sulphonium salts, but have the ortho-quinonoid structure (VIII):



It is interesting to observe, however, that the mercuric iodide compound which is described in a previous paragraph undoubtedly has the sulphonium structure, hence it appears that the salts of *S*-methylphenazothionium may exist in either form. The further

study of these salts has been abandoned on account of the difficulty of obtaining sufficient quantities of the base.

In conclusion, we desire to thank the Research Fund Committee of the Society for a grant which has defrayed the expense of these experiments.

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UNIVERSITY COLLEGE.

LXXVII.—*The Resolution of Externally Compensated Acids and Bases.*

By WILLIAM JACKSON POPE and JOHN READ.

CONSIDERABLE differences in behaviour are observed in different cases when an externally compensated base is crystallised with one-half an equivalent proportion of an optically active acid for the purpose of effecting its resolution into optically active components by the method of Pope and Peachey (Trans., 1899, **75**, 1066).

The crystallisation with rather less than one-half an equivalent proportion of optically active acid sometimes leads to an easy and rapid separation of the optically active components of the base. This kind of behaviour has been frequently observed, and as good examples of its occurrence may be mentioned the resolution of tetrahydroquinaldine (Pope and Peachey, Trans., 1899, **75**, 1066) and tetrahydro-*p*-toluquinaldine (Pope and Rich, Trans., 1899, **75**, 1093) by means of *d*- α -bromocamphor- π -sulphonic acid. Crystallisation of the externally compensated base with rather less than one-half an equivalent of the optically active acid (*dA*)—some other acid being present in sufficient quantity to retain the excess of base in solution—leads to the separation of the salt of the lævo-base (*lBdA*) in so pure a condition that one recrystallisation is sufficient to free it completely from mechanically adhering impurities. Under the conditions prevailing in the solution, equilibrium is established when the greater part of the optically active acid has separated with the lævo-base as the sparingly soluble salt, *lBdA*, and none crystallises as the more soluble salt, *dBdA*. In instances of this kind it must be concluded that no tendency exists towards the formation of solid solutions between the partly enantiomorphously related salts, *lBdA* and *dBdA*. In other resolutions, in which equivalent proportions of active acid and externally compensated

base are used, the two salts, *l*BdA and *d*BdA, may be seen to separate side by side with no tendency towards mutual solution. Thus, on crystallising Goldschmiedt's "tetrahydropapaverine"—which Pyman has recently shown to be a dihydropapaverine (Trans., 1909, **95**, 1610)—with *d*- α -bromocamphor- π -sulphonic acid, the salt *l*BdA separates in crystalline needles entangled with the gummy salt, *d*BdA (Pope and Peachey, Trans., 1898, **73**, 893).

In other cases, crystallisation in the manner just referred to leads to an immediate partial separation, which must be followed by a long and tedious fractional crystallisation before a pure salt of one component of the externally compensated base is obtained. This second kind of behaviour has not been previously distinguished in kind from the first; its occurrence is well illustrated in the crystallisation of externally compensated sodium 1-methylcyclohexylidene-4-acetate with rather less than one-half an equivalent of brucine hydrochloride (Perkin, Pope, and Wallach, Trans., 1909, **95**, 1790). The brucine salt of the *l*ævo-acid is less soluble than that with the dextro-acid, and exhibits the specific rotatory power $[\alpha]_D - 58.4^\circ$ in dilute alcohol. In one particular experiment, in which rather less than one-half an equivalent of brucine hydrochloride was crystallised with the externally compensated sodium salt, the first separation, which contained 80 per cent. of the added brucine, exhibited the specific rotatory power $[\alpha]_D - 50.9^\circ$; it thus consisted of about 84 per cent. of the salt *l*BdA, and 16 per cent. of *d*BdA. By prolonged fractional crystallisation, small proportions only of the component salts could be isolated; the crystallisation of the two salts, *l*BdA and *d*BdA, under the conditions stated, as a mixture which could only be slowly and partially resolved by fractional crystallisation, indicates that the two salts are mutually soluble in the solid state, and form solid solutions one in the other.

Kipping and Pope have quoted several cases (Trans., 1897, **71**, 989) in which two enantiomorphously related substances tend to crystallise together, not as definite racemic compounds, but merely as solid solutions of the one in the other or as interpenetration twin crystals, and, for the purpose of distinguishing these from truly racemic compounds, have termed them pseudoracemic mixtures. Other cases of pseudoracemism were subsequently described by Fock (*Zeitsch. Kryst. Min.*, 1899, **31**, 479), and the equilibrium conditions for racemic, partially racemic, and pseudoracemic substances in contact with their solutions have been defined by Roozeboom (*Zeitsch. physikal. Chem.*, 1899, **28**, 494).

From the above discussion and a consideration of the experimental facts, it is concluded that three kinds of behaviour must

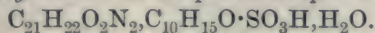
be distinguished when an externally compensated base (or acid) is crystallised with an optically active acid (or base). (1) The two salts, $dAdB$ and $lAdB$ (or $dAdB$ and $dAlB$), may crystallise separately with no tendency to form solid solutions one in the other; in this case the resolution by crystallisation or by Pope and Peachey's method proceeds with comparative ease. (2) The two salts, $dAdB$ and $lAdB$, combine in equimolecular proportion to form a partly racemic compound which cannot be separated by crystallisation; this type of case was discovered by Ladenburg, and has been well characterised by him (*Annalen*, 1909, **364**, 227). (3) The two salts, $dAdB$ and $lAdB$, in accordance with the new type of case now distinguished, form solid solutions one in the other which can only be partially separated by prolonged fractional crystallisation; such cases involve the formation of pseudo- and partially racemic mixtures corresponding to the formation of the pseudoracemic mixtures of two enantiomorphously related substances first distinguished by Kipping and Pope.

The distinction between the types of case (1) and (3) is of great practical importance, and we propose to investigate a number of cases in which these types are concerned.

π -Camphorsulphonic Acid.

Dextro- and lævo-bromocamphor were converted into the corresponding *d*- and *l*- α -bromocamphor- π -sulphonic acids, and the ammonium salts of the latter reduced in the manner described by Kipping and Pope (*Trans.*, 1895, **69**, 358). The crude ammonium salts of the enantiomorphously related π -camphorsulphonic acids were then treated with baryta in the usual way, and ultimately converted into solutions of the free acids (*Trans.*, 1898, **73**, 895); the concentrations of these aqueous solutions were determined by titration, and the corresponding strychnine salts prepared by crystallisation with the calculated quantities of the base.

Strychnine d-Camphor- π -sulphonate,



This salt is sparingly soluble in cold water or alcohol, dissolves readily in chloroform, and is only slightly soluble in other common solvents. It separates in aggregates of long, colourless, transparent prisms on cooling its hot aqueous alcoholic solution, and does not melt at 225° ; the crystals become opaque and very hygroscopic after heating at 150° :

0.1231 * gave 0.2869 CO_2 and 0.0763 H_2O . C = 63.56; H = 6.94.

* Air-dried.

0.9043 lost 0.0270 at 150°. $\text{H}_2\text{O} = 2.99$.

$\text{C}_{31}\text{H}_{38}\text{O}_6\text{N}_2\text{S}\cdot\text{H}_2\text{O}$ requires $\text{C} = 63.65$; $\text{H} = 6.90$;

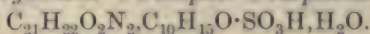
$1\text{H}_2\text{O} = 3.08$ per cent.

The following determinations of rotatory power were made, the weights stated being in each case made up to 20.05 c.c. with solvent and the solution examined in a 2-dcm. tube:

Solvent.	Weight (in gram)	α_D	$[\alpha]_D$
Alcohol	0.1050	+0.25°	+23.9°
"	0.1084	+0.26	+24.0
"	0.1042	+0.24	+23.1
Chloroform	0.1066	+0.24	+22.6
Water	0.1067	+0.12	+11.3

From the last stated value the molecular rotatory power of the salt in aqueous solution is calculated as $[\text{M}]_D + 66.0^\circ$.

Strychnine 1-Camphor- π -sulphonate,



This salt crystallises from its solution in hot dilute alcohol in long, transparent, colourless needles, and does not melt at 225°. It is sparingly soluble in water and alcohol, but more freely soluble in chloroform; its solubility is, however, markedly greater in the various solvents than that of strychnine *d*-camphorsulphonate:

0.0993 * gave 0.2317 CO_2 and 0.0635 H_2O . $\text{C} = 63.63$; $\text{H} = 7.16$.

0.9779 lost 0.0202 at 150°. $\text{H}_2\text{O} = 2.07$.

$\text{C}_{31}\text{H}_{38}\text{O}_6\text{N}_2\text{S}\cdot\text{H}_2\text{O}$ requires $\text{C} = 63.65$; $\text{H} = 6.90$;

$1\text{H}_2\text{O} = 3.08$ per cent.

The following determinations of rotatory power were made with the air-dried salt under the same conditions as before:

Solvent.	Weight (in gram).	α_D	$[\alpha]_D$
Alcohol	0.1036	-0.50°	-48.4°
Chloroform	0.1091	-0.69	-63.4
Water	0.1006	-0.51	-50.8

From the last value the molecular rotatory power of the salt in dilute aqueous solution is calculated as $[\text{M}]_D - 296.7^\circ$.

Ammonium d- and l-Camphor- π -sulphonates, $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{SO}_3\cdot\text{NH}_4$.

A number of salts of externally compensated π -camphorsulphonic acid have been described by Kipping and Pope (Trans., 1893, **63**, 574), together with a number of derivatives of the optically active acids; hitherto, however, no salts of the pure optically active acids have been examined. The solutions of the optically active acids prepared by reduction of the ammonium α -bromo- π -camphor-

sulphonates as above described are not sufficiently pure to yield at once pure samples of the very soluble ammonium camphor- π -sulphonates, but the latter salts are readily obtained in a state of high purity from the strychnine salts just above described. In this and a number of other cases in which an optically active acid yields very soluble salts with mineral bases, it is convenient to purify the acid by the aid of some alkaloid with which it forms a sparingly soluble salt. The ammonium *d*- and *l*-camphor- π -sulphonates are readily obtained by treating their strychnine salts with ammonia, extracting the filtered aqueous solution with chloroform, evaporating to dryness, and subsequently crystallising from alcohol; they crystallise from alcohol in long, colourless needles, and are extremely soluble in cold water, but less so in alcohol. The following results were obtained with ammonium *d*-camphor- π -sulphonate:

0.0987 gave 0.1750 CO₂ and 0.0674 H₂O. C=48.36; H=7.64.

C₁₀H₁₉O₄NS requires C=48.14; H=7.68 per cent.

The following determinations of rotatory power were made with salt dried at 100°; the solutions were made up to 20.05 c.c. with solvent, and examined in 2-dcm. tubes:

Solvent.	Weight (in gram).	α_D .	$[\alpha]_D$.
Alcohol	0.1033	+0.83°	+80.5°
Water	0.5010	+3.40	+68.0
"	0.3038	+2.01	+66.3
"	0.1071	+0.74	+69.1
"	0.1051	+0.72	+68.7

From the last two determinations the mean molecular rotatory power of the salt in dilute aqueous solution is calculated as $[M]_D + 171.6^\circ$.

The following determinations were made under similar conditions with samples of ammonium *l*-camphor- π -sulphonate dried at 100°.

Solvent.	Weight (in gram).	α_D .	$[\alpha]_D$.
Alcohol	0.1077	-0.86°	-80.1°
Water	0.5003	-3.41	-68.3
"	0.5033	-3.43	-68.3
"	0.3024	-2.07	-68.6
"	0.3028	-2.03	-67.2
"	0.1038	-0.71	-68.6
"	0.1023	-0.71	-69.6

The mean molecular rotatory power in dilute aqueous solution, calculated from the last two determinations, is $[M]_D - 172.0^\circ$. This latter value agrees well with the value $[M]_D + 171.8^\circ$ just given above for ammonium *d*-camphor- π -sulphonate, and, taking the mean of the values for the two salts, the molecular rotatory power of the optically active camphor- π -sulphonic ion appears to have the

value $[M]_D = 171.8^\circ$. This number should be one-half the arithmetic mean of the molecular rotatory powers of the strychnine salts of *d*- and *l*-camphor- π -sulphonic acid in dilute aqueous solution, namely, $(66.0^\circ + 296.7^\circ)/2 = 181.3^\circ$; the agreement is probably good, considering the high values of the molecular weights concerned.

*Resolution of Externally Compensated Ammonium
Camphor- π -sulphonate.*

The fact that the two salts, strychnine *d*- and *l*-camphor- π -sulphonate, possess very different solubilities, suggests that the externally compensated acid could be resolved by crystallisation with strychnine. Solutions of the externally compensated acid were therefore prepared by mixing equivalent quantities of the aqueous solutions of the enantiomorphously related acids made as described above; strychnine was then dissolved in these solutions, and the fractions of salt which separated were examined polarimetrically.

In one experiment a solution containing 19.86 grams of externally compensated acid was partly neutralised by dissolving in it 13.9 grams of the alkaloid, namely, 3 per cent. less than one-half an equivalent of strychnine. On cooling, a deposit of 20 grams of a salt, which crystallised in long, colourless needles, was obtained instead of the calculated amount of 23.8 grams; 0.1002 of this salt, made up to 20.05 c.c. with alcohol, gave $\alpha_D + 0.21^\circ$ in a 2-dcm. tube, whence $[\alpha]_D + 21.8^\circ$. After once recrystallising, the value became $[\alpha]_D + 24.4^\circ$. As under similar conditions the specific rotatory power of pure strychnine *d*-camphor- π -sulphonate is $[\alpha]_D + 24.0^\circ$, it is clear that the solution of the externally compensated acid had deposited almost the whole of the contained strychnine as its *d*-camphor- π -sulphonate. On subsequently adding to the mother liquor, containing the whole of the *l*-acid, sufficient strychnine to combine with all the acid present, a large deposit of strychnine *l*-camphor- π -sulphonate was obtained, which, on recrystallisation, at once yielded the latter salt in a state of purity.

It is thus evident that the resolution of externally compensated camphor- π -sulphonic acid by means of strychnine is easily effected by the method of Pope and Peachey, and that the two salts, *l*B*d*A and *l*B*l*A, of which the formation is possible in the system, exhibit no tendency to form solid solutions one in the other. The resolution thus presents an example of the kind of behaviour referred to under (1) above.

In a recent paper Rewald has described the resolution of

externally compensated camphor- β -sulphonic acid by crystallisation with brucine (*Ber.*, 1909, **42**, 3136), and remarks that this constitutes the first resolution of externally compensated camphor into its optically active components; this statement is, however, incorrect, first, because camphor- β -sulphonic acid has not yet been converted into camphor, and, secondly, because the resolution of externally compensated camphor has been previously effected. Externally compensated camphoroxime was resolved into its optically active components by Pope (*Trans.*, 1899, **75**, 1105), and Forster had previously shown (*Trans.*, 1897, **71**, 199) that camphor could be regenerated from its oxime; more recently Lapworth has obtained camphor by hydrolysing its oxime by means of formaldehyde (*Trans.*, 1907, **91**, 1133).

The mode of resolution just described was also applied to the mixture of *d*- and *l*-camphor- π -sulphonic acids obtained by sulphonating either ordinary or externally compensated camphor with chlorosulphonic acid as described by Kipping and Pope (*Trans.*, 1893, **63**, 552). After treating the sulphonation product with ice and expelling as much of the hydrogen chloride as possible on the water-bath, the sulphuric acid was removed as barium salt, and the remaining hydrochloric acid with silver hydroxide. The barium was precipitated by addition of the exact quantity of sulphuric acid requisite, and the acid solution warmed with zinc oxide; on concentrating the filtrate a crystalline zinc salt was obtained, which was decolorised by crystallisation from hot water. The zinc salt was apparently not a single substance, but its formation served to remove the colour from the sulphonic acid mixture; the free acid was obtained from it by precipitating with ammonia and hydrogen sulphide, boiling off the excess of the latter, and precipitating successively with baryta and sulphuric acid in the usual way. On concentration a viscid, gummy solution of the acid was obtained, which was neutralised by boiling with powdered strychnine; on cooling, a complex mixture of highly crystalline strychnine salts was obtained, from which, by prolonged fractional crystallisation, strychnine *d*- and *l*-camphor- π -sulphonates could be separated in a fairly pure state. Other strychnine salts were, however, present in considerable quantity, but neither of these was obtained as a pure substance.

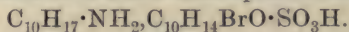
The product of the action of phosphorus pentachloride on the mixture of sodium salts obtained from the sulphonation of camphor as described above is known to contain externally compensated α - and β -chlorocamphenesulphonyl chlorides, and it has been suggested that these originate in secondary action between phosphorus pentachloride and the camphorsulphonyl chloride first

produced (Kipping and Pope, Proc., 1895, **11**, 57; Lapworth and Kipping, Trans., 1896, **69**, 1546). The results obtained in the above-described crystallisation with strychnine render this suggestion highly improbable, and indicate that the secondary products are formed during the original sulphonation; some confirmation of this latter view is afforded by the observation that on treating the ammonium camphor- π -sulphonates now described with phosphorus pentachloride and grinding the product with ice, the corresponding sulphonyl chlorides are at once obtained in the crystalline condition.

Crystallisation of Mixtures of Bornylamine and neoBornylamine with d- α -Bromocamphor- π -sulphonic Acid.

A considerable quantity of a mixture of bornylamine and *neo*-bornylamine was kindly handed to us by Dr. M. O. Forster; the hydrochloride prepared from this material gave a specific rotatory power of $[\alpha]_D + 1.3^\circ$ in dilute aqueous solution. Since under similar conditions the hydrochlorides of the pure bases give the values of $[\alpha]_D + 22.7^\circ$ and -39.0° respectively (Forster, Trans., 1898, **73**, 388), it follows that the original mixture of bases contained about twice as much bornylamine as *neobornylamine*. As the aqueous solution of the mixed hydrochlorides yielded a crystalline, sparingly soluble salt when treated with ammonium *d- α -bromocamphor- π -sulphonate*, it was decided to attempt the resolution of the mixture by recrystallisation of this salt. For purposes of comparison, pure *d*-bornylamine *d- α -bromocamphor-sulphonate* was first prepared.

d-Bornylamine d- α -Bromocamphor- π -sulphonate,



On mixing aqueous solutions of equivalent quantities of *d*-bornylamine hydrochloride and ammonium *d- α -bromocamphor-sulphonate*, a crystalline precipitate falls; on recrystallisation from dilute alcohol the salt is obtained as long, colourless, felted needles, melting at about 225° . The salt is sparingly soluble in hot water, and moderately so in hot aqueous alcohol:

0.7756 lost $0.0159 \text{ H}_2\text{O}$ at 100° . $\text{H}_2\text{O} = 2.06$. Theory for $1\text{H}_2\text{O} = 3.73$.

0.1010 * gave 0.1869 CO_2 and $0.0686 \text{ H}_2\text{O}$. Subtracting $\text{H}_2\text{O} = 2.06$. $\text{C} = 51.54$; $\text{H} = 7.52$.

$\text{C}_{20}\text{H}_{34}\text{O}_4\text{BrS}$ requires $\text{C} = 51.69$; $\text{H} = 7.38$ per cent.

0.1510, made up to 20.05 c.c. with alcohol, gave $\alpha_D + 1.22^\circ$ in a 2-dcm. tube, whence $[\alpha]_D + 81.0^\circ$.

* Air-dried,

0.1534, made up to 20.05 c.c. with water, gave $\alpha_D + 1.03^\circ$ in a 2-dcm. tube, whence $[\alpha]_D + 67.3^\circ$ and $[M]_D + 312^\circ$.

On mixing aqueous solutions of corresponding quantities of the mixture of bornylamine and *neobornylamine* hydrochlorides of specific rotatory power $[\alpha]_D + 1.3^\circ$, and ammonium *d*- α -bromocamphorsulphonate, a copious separation of crystalline salt occurred. After effecting the admixture in hot aqueous solution and adding just sufficient alcohol to keep the salt in solution at the boiling temperature, most of the salt separated, on cooling, in long, silky needles. This material exhibited a specific rotatory power in a 0.75 per cent. aqueous solution of $[\alpha]_D + 62.3^\circ$; on recrystallisation from a large quantity of hot dilute alcohol, the deposited salt, which represented a comparatively small fraction of the whole, gave the value $[\alpha]_D + 62.9^\circ$ in a 0.75 per cent. aqueous solution. A calculation based on the known molecular rotatory powers of the basic bornylamine and *neobornylamine* ions and of the acidic bromocamphorsulphonic ion indicates that the salts of the above rotatory powers consist of between two-thirds and three-quarters of the bornylamine salt; from the practical identity of the rotatory powers of the two samples of mixed salt it is to be concluded that no appreciable separation had been effected by the crystallisation.

The conclusion that *d*-bornylamine and *d-neobornylamine* *d*- α -bromocamphorsulphonates cannot be readily separated by crystallisation is extended by the following observations on the fractional deposition of mixtures of the two salts. An aqueous solution of 190 grams of the mixture of bornylamine and *neobornylamine* hydrochlorides was treated with rather more than the corresponding amount (330 instead of 325 grams) of ammonium *d*- α -bromocamphorsulphonate, the latter salt being added in portions; after each addition sufficient alcohol was added to the hot aqueous solution to effect the complete solution of the deposited salt, and crystallisation was allowed to occur by cooling. A first addition of 100 grams of the ammonium salt caused the deposition, after cooling, of 137 grams of bromocamphorsulphonate in place of the theoretical 141 grams; in a 0.75 per cent. alcoholic solution this fraction gave the specific rotation of $[\alpha]_D + 63.0^\circ$. On recrystallising this material from dilute alcohol, the fraction deposited gave $[\alpha]_D + 60.3^\circ$ in an alcoholic solution of the same concentration as before; on crystallising the latter again from its mother liquor, salt giving the value $[\alpha]_D + 64.4^\circ$ was deposited, and from the mother liquor a fraction giving the value $[\alpha]_D + 62.3^\circ$ was separated by concentration.

To the solution from which the above-mentioned 137 grams of salt had been removed, a further 50 grams of ammonium salt were

added, and a second large deposit obtained; this gave the value $[\alpha]_D + 58.4^\circ$ in a 0.75 per cent. alcoholic solution. To the residual solution, 20 grams of ammonium salt were next added; this led to the deposition of 28 grams, instead of the theoretical 28.2 grams, of salt; the latter gave the value $[\alpha]_D + 55.7^\circ$ in 0.75 per cent. alcoholic solution. The next two additions, each of 50 grams, of ammonium salt caused the deposition of fractions having the specific rotations of $[\alpha]_D + 61.8^\circ$ and 64.0° respectively. A sixth addition, of 40 grams, and a seventh, of 20 grams, of ammonium salt resulted in deposits giving the values $[\alpha]_D + 64.5^\circ$ and 35.3° respectively; the latter consisted principally of *neobornylamine d- α -bromocamphorsulphonate*, but was very small in quantity. As 330 grams of ammonium salt had now been added, whilst only 325 were required, the mother liquor was evaporated; a mixture of ammonium *d-bornylamine* and *d-neobornylamine d- α -bromocamphorsulphonates* was deposited, which, when recrystallised to remove the ammonium salt, yielded a small quantity of salt of the mixed organic bases having the specific rotatory power $[\alpha]_D + 63.7^\circ$.

These observations indicate clearly that, so far as crystallisation and separation are concerned, *d-bornylamine* and *d-neobornylamine* are isomorphously replaceable in their *d- α -bromocamphor- π -sulphonates*. The mixture of bornylamine and *neobornylamine bromocamphorsulphonates*, which is scarcely altered in composition by fractional crystallisation, contrasts strongly with the mixture of strychnine *d-* and *l-camphor- π -sulphonates*, which can be sharply separated by one crystallisation or by one fractional precipitation. The general conclusion is therefore to be drawn that the two non-enantiomorphously related salts, the *d- α -bromocamphor- π -sulphonates* of *d-bornylamine* and *d-neobornylamine*, form solid solutions one in the other, and that their degree of mutual miscibility in the solid state is so considerable that no effective separation is obtainable by any ordinary fractional crystallisation.

Incidentally, it may be remarked that unsuccessful attempts were made to resolve this particular mixture of bornylamine and *neobornylamine* by crystallisation with other optically active acids. The salt formed with *d-camphor- β -sulphonic acid* is too soluble in the ordinary solvents to allow of its fractional crystallisation. The normal tartrate separates as a gelatinous mass from acetone, benzene, and chloroform, and is very soluble in water; the acid tartrate is a colourless, crystalline substance, which is very sparingly soluble in the ordinary solvents.

Mixtures of d-Menthylamine and d-isomenthylamine Hydrochlorides.

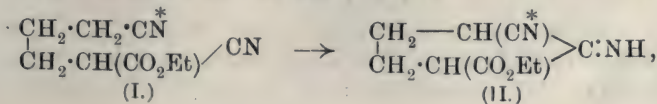
Whilst *d*-menthylamine and *d*-isomenthylamine hydrochlorides have the specific rotatory powers of $[\alpha]_D -36.6^\circ$ (Kipping and Tutin, *Trans.*, 1904, **85**, 69) and $+17.24^\circ$ (Wallach, *Annalen*, 1893, **276**, 326) respectively, a sample of *d*-menthylamine hydrochloride obtained from Schuchardt gave the value $[\alpha]_D -21.6^\circ$; all these constants were determined in dilute aqueous solution. On crystallising the latter sample repeatedly from water, the major portion of the substance being separated in each case, the successive deposits gave the values of $[\alpha]_D -27.4^\circ$, -30.1° , and -30.8° respectively. Three crystallisations of the last fraction from ethyl acetate, in which the substance is sparingly soluble, gave separations having the specific rotatory powers $[\alpha]_D -31.82^\circ$, -33.8° , and -35.1° respectively. Although repeated crystallisation of the mixture of *d*-menthylamine and *d*-isomenthylamine hydrochlorides is capable of ultimately yielding a pure sample of the former salt, it must be concluded from the difficulty with which the separation proceeds that the two salts crystallise together in the form of solid solutions.

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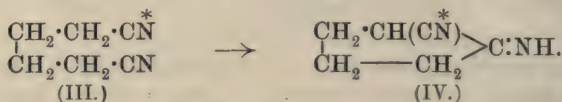
LXXVIII.—*The Formation and Reactions of Imino-compounds. Part XII. The Formation of Imino-derivatives of cyclopentane from Open-chain Mononitriles.*

By ALEC DUNCAN MITCHELL and JOCELYN FIELD THORPE.

It has been already shown that the five-carbon alicyclic ring is readily formed when a dinitrile having the two nitrile groups separated by four carbon atoms is treated with an alcoholic solution of sodium ethoxide or of an alkaline sodium derivative. Thus, ethyl $\alpha\delta$ -dicyanovaleate (I) passes in this manner into ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (II) (*Trans.*, 1909, **95**, 696):



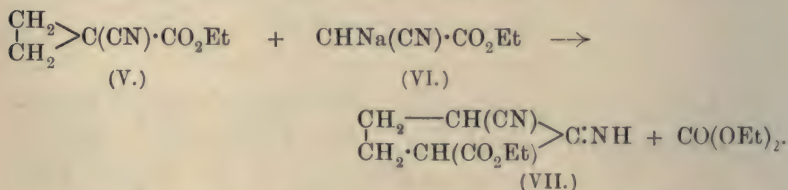
and $\alpha\delta$ -dicyanobutane (III) into 1-imino-2-cyanocyclopentane (IV) (Trans., 1909, 95, 685):



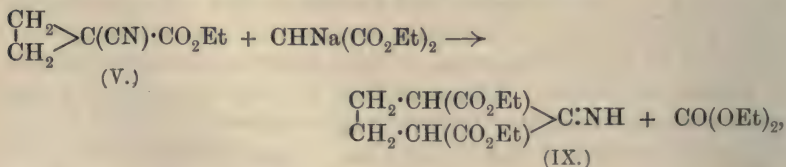
In both these cases, however, as indeed in all the reactions leading to the formation of imino-compounds described in this series up to the present, a second nitrile group marked in the above cases thus (*) was always present. This second nitrile group apparently played no part in the reaction, and it was with the object of showing that this second nitrile group is not essential to the reaction that the present experiments were undertaken.

It is evident that this method for closing the five-carbon ring would be of greater value for synthetic purposes if it could be shown that groups of similar character to the nitrile group, as, for example, the carbethoxy-group (CO_2Et), the phenyl group, etc., had no deterrent effect on the formation of the cyclic imino-compound. We therefore decided to settle this point by carrying out a series of experiments similar to those described in Part IX (Trans., 1909, 95, 687).

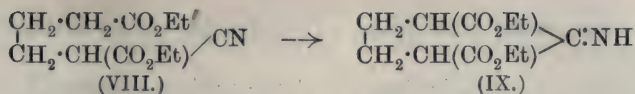
In that case it was shown that ethyl 1-cyanocyclopropane-1-carboxylate (V) condenses with the sodium compound of ethyl cyanoacetate (VI), yielding ethyl carbonate and ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (VII), thus:



If, therefore, the sodium compound of ethyl malonate is used instead of ethyl sodiocyanoacetate, the reaction might be expected to proceed in accordance with the following scheme:

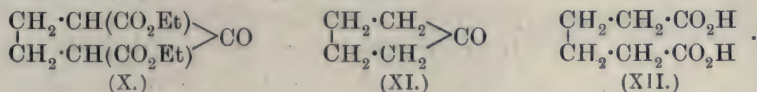


that is, provided the second nitrile group played no part in the reaction, and that there was just as great a tendency for a compound of the type (VIII) to react thus:



as for the dinitrile represented by formula (I).

As a matter of fact, the reaction proceeds in both cases in much the same manner, and a good yield of *ethyl 2-iminocyclopentane-1:3-dicarboxylate* (IX) can be obtained by the condensation given above, ethyl carbonate being formed at the same time. Ethyl 2-iminocyclopentane-1:3-dicarboxylate (IX) readily reacts with cold hydrochloric acid, giving *ethyl cyclopentan-1-one-2:5-dicarboxylate* (X), from which either *cyclopentanone* (XI) can be prepared by distillation with dilute sulphuric acid, or *adipic acid* (XII) can be produced by the action of alkalis:



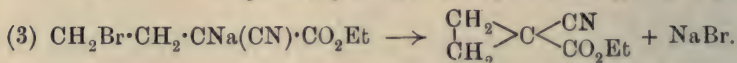
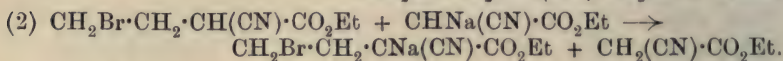
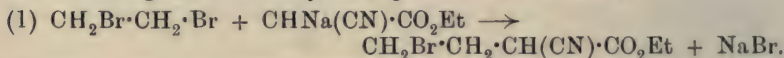
This is therefore another instance in which a carbethoxy-group is eliminated as ethyl carbonate from an open-chain compound before it passes into the five-membered ring. Several other cases of the same kind are in course of investigation, and will shortly be published. In every case the formation of the ring is accompanied either by the elimination of a carbethoxy-group in this manner, or by the elimination of an acetyl group, where such occurs, as ethyl acetate. There can be no question that such elimination is due to spatial considerations, or, in other words, that the carbon atoms of the *cyclopentane* ring cannot under ordinary conditions carry two carbethoxyl groups or a carbethoxy-group and an acetyl group on the same carbon atom.

The formation of ethyl 1-cyanocyclopropane-1-carboxylate (V) for use in these experiments was effected in the manner described by Carpenter and Perkin (*Trans.*, 1899, **75**, 921), that is, by the interaction of ethylene dibromide and ethyl sodiocyanoacetate, the cyclic ester being purified by distillation in a current of steam and subsequent fractional distillation.

Experiments on the condensation of this product with ethyl sodiomalonate always gave a quantity of an insoluble yellow sodium compound, the properties of which are described in the experimental portion. The empirical formula of the parent substance derived from this sodium compound by the action of acids seemed to suggest that its formation must be due to the presence of ethyl cyanoacetate in the cyclic ester used, a view which was subsequently shown to be correct by experiment, for it was found that when ethyl 1-cyanocyclopropane-1-carboxylate was freed from ethyl cyanoacetate by a method described later, no formation of an insoluble

sodium compound took place on condensing it with ethyl sodiomalonate.

It has been frequently shown that the sodium compound of ethyl cyanoacetate, when treated with water, does not regenerate ethyl cyanoacetate, but passes at once into the soluble sodium salt of cyanoacetic acid, and the question therefore arises how is it possible that ethyl cyanoacetate can be present in the cyclic ester when it is remembered that equivalent amounts of sodium and ethyl cyanoacetate are employed. The explanation is that the reaction between ethylene dibromide and ethyl sodiocyanoacetate takes place in three stages, which may be represented as follows:



Ethyl 1-cyanocyclopropane-1-carboxylate boils at 212° , and ethyl cyanoacetate at 208° , under the same pressure. It is therefore exceedingly difficult to separate these substances completely by fractional distillation. It will be noticed that the analysis of ethyl 1-cyanocyclopropane-1-carboxylate given by Carpenter and Perkin (*loc. cit.*, p. 925) indicates the presence of some ethyl cyanoacetate in their product. Ultimately it was found that the cyclic ester could be entirely freed from ethyl cyanoacetate by treating the mixture of the two substances with an amount of sodium ethoxide in alcoholic solution slightly in excess of the amount required to combine with the ethyl cyanoacetate present, this amount being determined by a carbon estimation of the mixture. The alcoholic solution was then poured into water, when the sodium compound of ethyl cyanoacetate was converted into the soluble sodium salt of cyanoacetic acid, and the pure cyclic ester was precipitated.

The pure ethyl salt, when condensed in the manner given above with the sodium compound of ethyl malonate, does not yield any of the insoluble sodium compound, and it is therefore evident that the formation of this substance is entirely due to the presence of ethyl cyanoacetate.

EXPERIMENTAL.

Condensation of Ethyl 1-Cyanocyclopropane-1-carboxylate containing Ethyl Cyanoacetate with Ethyl Sodiomalonate.

The ethyl 1-cyanocyclopropane-1-carboxylate used for the purpose of this condensation was prepared by Carpenter and Perkin's method (*Trans.*, 1899, **75**, 924), a large amount having been

obtained as a by-product during the preparation of ethyl 2-imino-3-cyanocyclopentane-1-carboxylate described in Part IX of this series (Trans., 1909, **95**, 696). The condensation was effected in the usual manner, 11.5 grams of sodium being dissolved in 150 grams of alcohol, 80 grams of ethyl malonate added, and the solution mixed with 70 grams of ethyl 1-cyanocyclopropane-1-carboxylate. After the mixture had been heated on the water-bath for fifteen minutes, the solution began to assume a yellow colour, and a crystalline substance slowly separated. When the separation of this substance appeared to be complete, which was usually the case after the heating had been continued for one hour, the salt was collected, washed with hot alcohol, in which it was found to be quite insoluble, and dried on a porous plate. Two analyses of the product, purified by boiling with absolute alcohol and filtering, gave 15.1 and 15.18 per cent. of sodium respectively. Too much trust cannot, however, be placed in these figures, as we have reason to think that the salt contained some sodium carbonate, from which it was not found possible to free it.

The quantity of the sodium compound formed in the above experiment was 10 grams. It dissolves in water, yielding a strongly alkaline solution, from which hydrochloric acid or, better, acetic acid precipitates a crystalline solid. This solid crystallises from ethyl alcohol in large, colourless needles, melting at 206° , and forming a deep red liquid, which ultimately chars with evolution of gas:

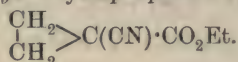
(1) 0.1759 gave 0.3725 CO_2 and 0.0771 H_2O . $\text{C}=57.76$; $\text{H}=4.85$.

(2) 0.1708 „ 0.3626 CO_2 „ 0.0739 H_2O . $\text{C}=57.90$; $\text{H}=4.81$.

0.2090 „ 18 c.c. N_2 at 13° and 747 mm. $\text{N}=10.1$.

$\text{C}_{14}\text{H}_{14}\text{O}_5\text{N}_2$ requires $\text{C}=57.93$; $\text{H}=4.8$; $\text{N}=9.7$ per cent.

The compound gives a red colour with ferric chloride in alcohol solution. It is soluble in aqueous alkalis and in solution of alkaline carbonates, from which solutions acids reprecipitate the original substance. It dissolves in concentrated hydrochloric acid, and is precipitated unchanged on the addition of water. When boiled with aqueous potassium hydroxide, ammonia is evolved, and the solution, on acidifying, yields a solid acid, which crystallises from alcohol in small needles, melting and decomposing at 159° . These compounds are still under investigation. Subsequent experiments showed that their formation had nothing to do with the condensation of ethyl 1-cyanocyclopropane-1-carboxylate with the sodium compound of ethyl malonate, but that they are produced by the action of some ethyl cyanoacetate contained in the cyclic ester.

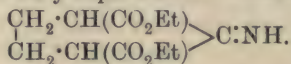
Ethyl 1-Cyanocyclopropane-1-carboxylate,

The method adopted in order to prepare this substance free from ethyl cyanoacetate was as follows. In the first instance, an estimation of carbon was made in order to give some indication of the amount of ethyl cyanoacetate present in the product, which had been previously carefully fractionated. The difference in the percentage of carbon present in the two components of the mixture is 7.3, being 53.1 per cent. for ethyl cyanoacetate and 60.4 per cent. for ethyl 1-cyanocyclopropane-1-carboxylate. In the actual experiment described, the percentage of carbon was found to be 59.53. This would mean that the mixture contained 12 per cent. of ethyl cyanoacetate, and 100 grams of the impure cyclic ester were therefore added to a solution of 2.2 grams of sodium dissolved in 50 grams of alcohol, the solution being immediately diluted with water. The oil which separated was then extracted and distilled. It boiled at 212°/763 mm.:

0.1934 gave 0.4282 CO₂ and 0.1131 H₂O. C = 60.36; H = 6.49.

C₇H₉O₂N requires C = 60.4; H = 6.5 per cent.

Care must be taken in the above experiment that excess of sodium ethoxide is not present. It was found that when a large quantity of the ethoxide was used, the whole of the cyclic ester was hydrolysed to the corresponding cyano-acid. It is probable that the hydrolysis takes place on pouring the alkaline solution into water, but it could not be prevented even by pouring the alcoholic solution on ice.

Ethyl 2-Iminocyclopentane-1:3-dicarboxylate,

This substance is formed by the condensation of ethyl sodio-malonate and ethyl 1-cyanocyclopropane-1-carboxylate in the following manner. 9.2 Grams of sodium are dissolved in 120 grams of alcohol, and the solution mixed with 64 grams of ethyl malonate, 56 grams of ethyl 1-cyanocyclopropane-1-carboxylate being subsequently added. The mixture is then heated on the water-bath for two hours, when it is poured into water. The oil which separates is extracted by ether, and the residue left after evaporating the ether distilled in a current of steam until no oily drops appear any longer in the distillate.

Unchanged ethyl malonate and ethyl carbonate passed over with

the steam, and were separated by extraction and fractional distillation. The residue, which was not volatile with steam, was extracted by ether and distilled. The whole quantity boiled constantly at $187^{\circ}/25$ mm., and consisted of a clear, fairly mobile oil without perceptible odour. It showed no signs of crystallising:

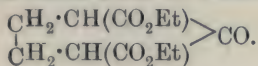
0.1559 gave 0.3314 CO_2 and 0.1070 H_2O . $\text{C}=57.98$; $\text{H}=7.53$.

0.1993 „, 11.2 c.c. N_2 at 16° and 723 mm. $\text{N}=6.31$.

$\text{C}_{11}\text{H}_{17}\text{O}_4\text{N}$ requires $\text{C}=58.1$; $\text{H}=7.5$; $\text{N}=6.2$ per cent.

The imino-compound is immediately and completely soluble in concentrated hydrochloric acid. When dissolved in alcohol it gives no immediate colour with ferric chloride, but the solution after some time gradually becomes purple, owing, presumably, to the production of the corresponding ketone.

Ethyl cyclopentan-1-one-2:5-dicarboxylate,



This substance is best prepared by mixing the liquid imino-compound with twice its volume of concentrated hydrochloric acid, and, after keeping the clear solution for five minutes, to pour it into twice its volume of boiling water, immediately cooling the solution as soon as all has been added. An oil separates, which, when extracted by ether, can be freed from any unchanged imino-compound by shaking with sodium carbonate solution in which the ketone dissolves. The sodium carbonate solution yields the pure ketone on being rendered acid and extracting with ether. It boils at $173^{\circ}/25$ mm., and is a clear, mobile liquid, giving in alcoholic solution an intense purple colour with ferric chloride. It was quite free from nitrogen:

0.1700 gave 0.3613 CO_2 and 0.1103 H_2O . $\text{C}=57.96$; $\text{H}=7.21$.

$\text{C}_{11}\text{H}_{16}\text{O}_5$ requires $\text{C}=57.9$; $\text{H}=7.0$ per cent.

cyclopentan-1-one-2:5-dicarbonylphenylide,

$$\begin{array}{c} \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NHPH}) \\ | \\ \text{CH}_2 \cdot \text{CH}(\text{CO} \cdot \text{NHPH}) \end{array} > \text{CO}.$$

A substance corresponding with this formula is formed when the ketone is boiled with an equal volume of aniline for one minute and the solution poured into dilute hydrochloric acid. It crystallises from hot alcohol, in which it is only sparingly soluble, in glistening plates, melting at 195° :

0.1067 gave 0.2766 CO_2 and 0.0548 H_2O . $\text{C}=70.70$; $\text{H}=5.70$.

$\text{C}_{19}\text{H}_{18}\text{O}_3\text{N}_2$ requires $\text{C}=70.8$; $\text{H}=5.6$ per cent.

The Products of Hydrolysis of Ethyl cyclopentan-1-one-2: 5-dicarboxylate.

(1) *cyclopentanone*.—This ketone is formed from ethyl *cyclopentan-1-one-2: 5-dicarboxylate* when it is mixed with an equal volume of concentrated sulphuric acid diluted with twice its volume of water, and, after the solution had been heated in a Geissler flask for half an hour, distilled in a current of steam. The *cyclopentanone* passes over with the steam, and was isolated by extracting the distillate with ether after saturation with ammonium sulphate. It was characterised by conversion into the semicarbazone, melting at 209° (Found, C=51.08; H=7.83. Calc., C=51.1; H=7.8 per cent.).

(2) *Adipic Acid*.—This acid is formed by the complete alkaline hydrolysis of ethyl *cyclopentan-1-one-2: 5-dicarboxylate*, and can be obtained in the following way. Two grams of the ethyl ester or of the corresponding imino-compound are boiled with aqueous potassium hydroxide until a test portion no longer deposits an oil on acidifying. The solution is then acidified and extracted with ether. The ethereal extract, after being dried, is evaporated free from ether, and the residue heated in a bath of sulphuric acid at 180° until the evolution of gas has ceased. The residue on recrystallisation yielded adipic acid, melting at 149° (Found, C=49.0; H=6.87. Calc., C=49.3; H=6.9 per cent.).

Much of the expense entailed by this research has been met by grants from the Government Grant Committee of the Royal Society, and from the Research Fund of the Chemical Society, for which we desire to express our indebtedness.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY,
SHEFFIELD.

LXXIX.—*The Constituents of the Flowers of Trifolium incarnatum.*

By HAROLD ROGERSON.

THE flowers of *Trifolium incarnatum*, Linné—the so-called “Carnation or Crimson Clover”—appear never to have been chemically examined. Inasmuch as the flowers of the common red clover (*Trifolium pratense*, Linné) have recently been made the

subject of a thorough investigation (Power and Salway, this vol., p. 231), it was deemed desirable also to examine those of the less widely cultivated "carnation clover," especially as the latter possess such very distinctive characters. It has thus been ascertained that the flowers of the two above-mentioned species of *Trifolium* exhibit appreciable differences with respect to their constituents, and a complete summary of the results of the present investigation is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the flowering tops of *Trifolium incarnatum*, which had been collected during the month of June from a field of the cultivated plant in Kent.

A portion (10 grams) of the dried material was first tested for the presence of an alkaloid, but the reactions obtained were very slight, and indicated the presence of not more than traces of such a substance.

Another portion (25 grams) of the dried material was successively extracted in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0·50 gram	=	2·00	per cent.
Ether	0·32	"	=	1·28 "
Chloroform	0·20	"	=	0·80 "
Ethyl acetate	1·03	grams	=	4·12 "
Alcohol	4·60	"	=	18·40 "
Water	1·29	"	=	5·60 "

Total... 7·94 grams = 31·76 per cent.

For the purpose of a complete examination, 94·35 kilograms of the flowers were collected. This material, after careful drying, amounted to 20·75 kilograms, or 22 per cent. of the original weight. The entire amount of this material was ground, and then extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a dark-coloured extract was obtained, which amounted to 6·35 kilograms.

Distillation of the Extract with Steam: Separation of an Essential Oil.

The whole of the above-mentioned extract was mixed with water, and steam passed through the mixture for several hours. The distillate (12 litres) contained some drops of oil floating on the surface. It was thoroughly extracted with ether, the ethereal liquid being dried, and the solvent removed, when 6 grams of an essential oil were obtained. The yield of the latter was equivalent

to 0.029 per cent. of the dried, or 0.006 per cent. of the fresh flowers.

This essential oil, when distilled under diminished pressure, passed over between 120° and $180^{\circ}/15$ mm. It was a pale yellow, mobile liquid, which darkened slightly on keeping, and possessed a strong, persistent odour. It gave a brown colour with ferric chloride, and a strong furfuraldehyde reaction. Its constants were as follows: $d_{20^{\circ}/20^{\circ}} = 0.9597$; $n_D - 1.48'$ in a 1-dcm. tube.

After the distillation of the extract with steam, as above described, there remained a dark-coloured aqueous liquid (A), together with a quantity of green, resinous material (B). These products were separated by filtration when cold, and the resin was washed repeatedly with hot water until nothing further was removed, the washings being added to the aqueous liquid.

Examination of the Aqueous Liquid (A).

Isolation of Benzoic and Salicylic Acids.

The aqueous liquid was repeatedly extracted with ether, the combined ethereal liquids concentrated to the volume of 1 litre, and then shaken with successive portions of aqueous ammonium carbonate. The alkaline liquids were united, acidified, and again extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A little resinous material was thus obtained, from which, by repeated treatment with light petroleum, a small amount of a crystalline product was extracted. The latter was recrystallised from water, when it separated in plates and needles, thus indicating it to be a mixture. For the purpose of effecting a separation of the acids, they were converted into their ethyl esters, the ethereal solution of which was first shaken with aqueous sodium carbonate to remove any unchanged acid, and subsequently with an aqueous solution of sodium hydroxide. On evaporating the ether, a small amount of an oily liquid was obtained, which possessed the odour of ethyl benzoate, and, on hydrolysis, yielded an acid which, when crystallised from water, separated in plates, melting at 121 — 122° . This substance was evidently benzoic acid, and its identity was confirmed by mixing it with a little of the latter acid, when the melting point remained unchanged.

The alkaline liquid obtained by shaking the ethereal solution of the above-mentioned esters with aqueous sodium hydroxide was boiled for some time and acidified, when a small amount of substance was obtained which, when crystallised from water, separated in needles, melting at 154 — 156° . This substance gave a violet coloration with ferric chloride, and evidently consisted of salicylic

acid, since its melting point remained unchanged when mixed with this acid.

The resinous material from which the benzoic and salicylic acids had been separated was further treated with a mixture of light petroleum and ether. On removing the solvent a very small amount of a crystalline substance was obtained, which, when recrystallised from water, separated in needles, melting and decomposing at 206—207°. This substance appeared to be *p*-coumaric acid, which, together with salicylic acid, has recently been shown to be a constituent of red clover flowers (*loc. cit.*). None of the above-mentioned acids was obtained in an amount sufficient for analysis.

Isolation of Quercetin, C₁₅H₁₀O₇.

The ethereal extract of the aqueous liquid, after being treated with ammonium carbonate as above described, was shaken with twelve successive portions of aqueous sodium carbonate. These alkaline liquids were separately acidified, and the resulting yellow precipitates collected, washed, and dried. They were then united to form five fractions, which were acetylated. The acetyl derivatives of the first four fractions, having been found to be identical, were united, and hydrolysed by heating with dilute sulphuric acid in aqueous alcohol. On subsequently removing the alcohol by distillation in a current of steam, a small amount (0.4 gram) of a yellow substance separated in small, yellow needles, which melted and decomposed at 305°. After drying at 135—140°, the substance was analysed:

0.1022 gave 0.2242 CO₂ and 0.0366 H₂O. C=59.8; H=3.9.

C₁₅H₁₀O₇ requires C=59.6; H=3.3 per cent.

A portion of the substance was again converted into its acetyl derivative by heating with acetic anhydride. On adding about an equal volume of light petroleum (b. p. 90—120°) to the hot solution, a crystalline product almost immediately separated, which melted at 195—196°. This substance, after drying at 110°, was analysed:

0.0920 gave 0.1962 CO₂ and 0.0350 H₂O. C=58.2; H=4.2.

C₁₅H₅O₇(CO·CH₃)₅ requires C=58.6; H=3.9 per cent.

From these results it is evident that the above-described yellow colouring matter was quercetin. It has previously been shown that this compound is contained in two other species of clover in the form of a glucoside, having been obtained by Perkin and Phipps (*Trans.*, 1904, **85**, 58) from white clover flowers (*Trifolium repens*), and quite recently by Power and Salway (*loc. cit.*, p. 244) from the flowers of the common red clover (*Trifolium pratense*).

Isolation of Pratol, C₁₆H₁₂O₄.

The final fraction of the above-mentioned sodium carbonate extracts of the ethereal liquid yielded, when acidified, a precipitate which could not be directly purified by crystallisation. It was therefore acetylated, and the acetyl derivative so obtained crystallised from a mixture of alcohol and ethyl acetate, when it separated in needles, melting at 166°. The amount of this substance was insufficient for analysis, but on comparing it with the acetyl derivative of pratol, C₁₆H₁₂O₄ (Power and Salway, *loc. cit.*, p. 233), the two compounds were found to be identical.

Isolation of a New Glucoside, Incarnatrin, C₂₁H₂₀O₁₂·3H₂O.

The original aqueous liquid (A), which had been repeatedly extracted with ether as above described, was shaken with many successive portions of amyl alcohol. These liquids were united, washed with water, and concentrated under diminished pressure to a volume of about 500 c.c., when, after some time, a yellowish-brown precipitate was deposited, which was collected and washed with light petroleum. By the further concentration of the amyl-alcoholic liquid, a much larger quantity of a yellow precipitate was obtained, which was similarly collected and washed. The final amyl-alcoholic filtrate was concentrated and treated with light petroleum, when a further small quantity of yellow product was obtained. Each of these precipitates was dissolved in a small amount of alcohol, and the solutions kept for some time, when small amounts of a crystalline product were obtained, which were finally united and crystallised from water. A quantity (0.4 gram) of a substance then separated in faintly yellow, prismatic needles, which softened at 165°, and decomposed at 242—245°. The substance was first dried in a vacuum, and then analysed:

0.1490 lost 0.0136 H₂O at 115—120°. H₂O = 9.1.

0.1354 * gave 0.2702 CO₂ and 0.0600 H₂O. C = 54.4; H = 4.9.

C₂₁H₂₀O₁₂·3H₂O requires H₂O = 10.4 per cent.

C₂₁H₂₀O₁₂ requires C = 54.3; H = 4.3 „

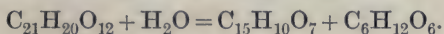
From these results it would appear that this substance possesses the formula C₂₁H₂₀O₁₂·3H₂O, but that a little of the water of crystallisation had been lost on drying in a vacuum.

The glucosidic character of this substance was established by heating a portion of it for about two hours with 2.5 per cent. aqueous sulphuric acid. On cooling, a yellow, crystalline substance was deposited, which yielded an acetyl derivative melting at

* Anhydrous substance.

195—196°. The aqueous acid liquid was treated with baryta for the removal of the sulphuric acid, filtered, and concentrated. It then yielded an osazone, which, after recrystallisation from dilute pyridine, melted at 203—205°.

It is evident from the above results that the substance under examination was a glucoside of quercetin, and that its hydrolysis can be represented by the following equation:



Hitherto, only two other glucosides appear to have been isolated which give quercetin and glucose on hydrolysis, namely, osyritrin, $\text{C}_{27}\text{H}_{28}\text{O}_{16} \cdot 3\text{H}_2\text{O}$ (m. p. 185°), which was first obtained by A. G. Perkin from Cape sumach (Trans., 1897, **71**, 1131), and quercimeritrin, $\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot 3\text{H}_2\text{O}$ (m. p. 247—249°), which has quite recently been isolated by the same investigator from cotton flowers (Trans., 1909, **95**, 2181). As there was a possibility of the above-described glucoside being identical with quercimeritrin, a specimen of the latter was kindly supplied by Professor A. G. Perkin for the purpose of comparison, but they were found to differ in their character. The glucoside obtained from *Trifolium incarnatum* is therefore a new compound, and it is proposed to designate it *incarnatrin*, with reference to the specific name of the plant.

Incarnatrin is hydrolysed by emulsin, and is therefore a β -glucoside. It dissolves slowly in concentrated sulphuric acid with a yellow colour, and the solution soon develops a green fluorescence.

The original aqueous liquid, after being freed from amyl alcohol by means of steam, was treated with an excess of a solution of basic lead acetate. A bulky, yellowish-brown precipitate was thus obtained, which was collected, well washed with water, then suspended in water, decomposed by hydrogen sulphide, and the mixture filtered. The resulting liquid, when concentrated, had a dark red colour, and appeared to contain only a small amount of tannic matter.

The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide in order to remove lead, and concentrated under diminished pressure. A syrupy liquid was thus obtained which evidently contained a quantity of sugar, for it readily reduced Fehling's solution, and yielded *d*-phenylglucosazone, melting at 205—206°.

Examination of the Resin (B).

This resin, as already indicated, represented that portion of the original alcoholic extract which was insoluble in water. At the ordinary temperature, it was a soft, green mass, and amounted to

856 grams. It was treated with hot alcohol, when a portion (88 grams) remained undissolved in the form of a hard, brown solid.

For the examination of the soluble portion of the resin, a quantity (192 grams) representing 1.59 kilograms of the original alcoholic extract was employed. This was mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with petroleum (b. p. 35—50°), ether chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract was a soft, dark green mass, amounting to 157 grams. It was dissolved in ether, and the ethereal liquid extracted with a solution of ammonium carbonate, which, however, removed nothing. On subsequently shaking the ethereal liquid with successive portions of aqueous potassium carbonate, a quantity of material was removed. The alkaline liquids thus obtained were therefore acidified and extracted with ether, when a small amount of substance remained undissolved. This substance, which was very sparingly soluble in ether, was collected, dissolved in dilute alcohol, and the solution treated with animal charcoal. On subsequently concentrating the solution, the substance separated in glistening laminae, which melted and decomposed at 235°, but the amount was not sufficient for its further examination.

The ethereal liquid, from which the above-mentioned substance had been removed by filtration, was washed, dried, and the solvent removed. A quantity of fatty acids was thus obtained, together with some resinous matter. In order to purify the acids, they were converted into their ethyl esters, and the latter distilled under diminished pressure. The esters were then hydrolysed, and the regenerated acids distilled under diminished pressure, when they passed over between 220° and 280°/15 mm. as a viscid liquid, which solidified on cooling to a white, crystalline mass. The acids thus obtained amounted to 16.5 grams, and they were examined in connexion with a similar product obtained from the petroleum extract after its hydrolysis.

The ethereal liquid which had been extracted with potassium carbonate, as above described, was subsequently shaken with a solution of sodium hydroxide, which, however, removed only a little resinous material.

Hydrolysis of the Petroleum Extract.

After extracting the ethereal solution of the petroleum extract with alkalis, as above described, the ether was evaporated, when a

quantity (90 grams) of a dark green, resinous mass was obtained. This was hydrolysed by heating with an alcoholic solution of potassium hydroxide, after which water was added, the alcohol removed, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was then washed, dried, and the solvent evaporated, when 30 grams of a dark yellow solid were obtained.

Isolation of Incarnatyl Alcohol, $C_{34}H_{69}\cdot OH$, and Hentriacontane, $C_{31}H_{64}$.

The above-mentioned solid, representing the unsaponifiable constituents of the petroleum extract, was dissolved in 1 litre of hot alcohol, and the solution allowed to cool, when a quantity (8 grams) of a sparingly soluble substance separated. This was collected, washed with a little alcohol, and dried, when it was found to consist chiefly of a hydrocarbon with a small amount of an oxygenated compound, which presumably was an alcohol. In order to effect their separation, 5 grams of the mixture were heated with an equal weight of phthalic anhydride for about two hours at 140° , the product being subsequently dissolved in a mixture of chloroform and ether, and the solution shaken with aqueous sodium carbonate. A solid compound then separated, which evidently was the sodium salt of an acid phthalic ester. This was hydrolysed with an alcoholic solution of potassium hydroxide, when, on cooling, a substance was deposited which, after recrystallisation from a mixture of ethyl acetate and alcohol, separated in needles, melting at $72-74^{\circ}$:

0.0784 gave 0.2370 CO_2 and 0.1024 H_2O . $C=82.4$; $H=14.5$.

$C_{34}H_{70}O$ requires $C=82.6$; $H=14.2$ per cent.

In order further to characterise this substance, a portion of it was heated with benzoyl chloride, the excess of the latter having been removed by heating the mixture with a little absolute alcohol and subsequent distillation with steam. The precipitated benzoyl derivative was then crystallised from alcohol, when it separated in small needles, melting at $58-60^{\circ}$.

From the above results it is evident that the substance $C_{34}H_{69}\cdot OH$ is identical with an alcohol previously obtained from the wax of the humble-bee by Sundwik (*Zeitsch. physiol. Chem.*, 1898, **26**, 58), who recorded its melting point as $74-75^{\circ}$, and that of its benzoyl derivative as 55° . As no name was assigned by Sundwik to this compound, it is proposed to designate it incarnatyl alcohol, with reference to the species of clover, *Trifolium incarnatum*, from which it has now been isolated.

The chloroform-ether liquid from which the *sodium incarnatyl phthalate* had separated was dried, and the solvent evaporated.

The residue thus obtained was heated with an alcoholic solution of potassium hydroxide in order to remove unchanged phthalic anhydride, when, on cooling, a small amount of a substance was deposited. This was collected, dried, and crystallised from ethyl acetate, when it separated in pearly leaflets, melting at 68° , and was identified as hentriacontane. (Found, $C=84.9$; $H=14.9$. Calc., $C=85.3$; $H=14.7$ per cent.)

Isolation of a Phytosterol, $C_{27}H_{46}O$.

The alcoholic liquid from which the above-described mixture of incarnatyl alcohol and hentriacontane had separated was concentrated to about half its volume, when a further quantity of solid was deposited. This was collected, and found to consist of a mixture of hentriacontane and a phytosterol. On concentrating the mother liquors, an additional quantity of substance was obtained, which, after crystallisation from a mixture of ethyl acetate and dilute alcohol, separated in fine, glistening needles, melting at $135-136^{\circ}$:

0.4994 lost $0.0248 H_2O$ at 110° . $H_2O=4.9$.

0.1056 * gave $0.3244 CO_2$ and $0.1160 H_2O$. $C=83.8$; $H=12.2$.

$C_{27}H_{46}O, H_2O$ requires $H_2O=4.5$ per cent.

$C_{27}H_{46}O$ requires $C=83.9$; $H=11.9$ per cent.

This substance is thus seen to agree in composition with a phytosterol, and it yielded the colour reaction of this class of compounds. A determination of its optical rotatory power gave the following result:

0.2478 of anhydrous substance, made up to 20 c.c. with chloroform, gave $\alpha_D -1.02'$ in a 2-dcm. tube, whence $[\alpha]_D -41.7^{\circ}$.

The acetyl derivative, when crystallised from acetic anhydride, separated in needles, melting at $124-125^{\circ}$.

0.1860, made up to 20 c.c. with chloroform, gave $\alpha_D -0.49'$ in a 2-dcm. tube, whence $[\alpha]_D -43.9^{\circ}$.

The final mother liquors, after the separation of the above-described phytosterol, were evaporated until all the alcohol was removed. The residue consisted of a semi-solid mass, which was distilled under diminished pressure, and then amounted to 9.4 grams. It was found to consist chiefly of liquid hydrocarbons, with some oxygenated substances, but from it there could be isolated only a very small quantity of an alcohol, which crystallised in leaflets, melting at 88° .

* Anhydrous substance.

Identification of the Fatty Acids.

The alkaline, aqueous solution of potassium salts, from which the substances described above had been removed by extraction with ether, was acidified and again extracted with ether, the ethereal solution being washed, dried, and the solvent removed. A quantity (9.3 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 220° and $280^{\circ}/15$ mm. As these acids distilled within the same range of temperature as those previously obtained, which existed in the flowers in the free state, for the purpose of their examination the two portions were mixed.

Twenty-five grams of the total mixed acids were converted into their lead salts, and the latter digested with ether, when a portion was dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 12.6 grams of liquid acids, whilst the insoluble portion gave 10.5 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 230° and $250^{\circ}/15$ mm. A determination of the iodine value gave the following result:

0.2358 absorbed 0.3745 iodine. Iodine value = 158.8.

This indicated that the liquid acids consisted of a mixture, containing some acid or acids of a higher degree of unsaturation than oleic acid.

In order to obtain more definite information respecting the composition of the above mixture, a quantity (7.5 grams) of it was oxidised with potassium permanganate according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, Vol. I, p. 360). The chief product of the oxidation was an acid melting at 156 — 158° , which analysis showed to be tetrahydroxystearic (sativic) acid (Found, C = 61.7; H = 10.5. Calc., C = 62.1; H = 10.3 per cent.). In addition to this acid, small amounts of dihydroxystearic acid (m. p. 125 — 127°) and hexahydroxystearic acid (m. p. 168 — 170°) were obtained.

The above results would therefore indicate that the unsaturated acids consisted chiefly of linolic acid, with smaller amounts of oleic and isolinolenic acids.

The Solid Acids.—These acids were fractionally crystallised from alcohol, when two fractions were obtained, which melted respectively at 50 — 52° and 55 — 57° .

Fraction 50—52°.—This fraction was analysed, with the following result:

0.1360 gave 0.3752 CO₂ and 0.1588 H₂O. C=75.2; H=12.9.

C₁₆H₃₂O₂ requires C=75.0; H=12.5 per cent.

C₁₈H₃₆O₂ " C=76.1; H=12.7 "

The above fraction thus appeared to consist of a mixture of palmitic and stearic acids.

Fraction 55—57°.—On recrystallising this fraction from glacial acetic acid, it yielded palmitic acid (m. p. 60—61°: Found, C=74.8; H=12.8. Calc., C=75.0; H=12.5 per cent.).

Ethereal Extract of the Resin.

Isolation of Trifolanol, C₂₁H₃₄O₂(OH)₂.

During the extraction of the resin with ether it was observed that a sparingly soluble substance had separated. This was collected, washed, and dried, when it amounted to 2.9 grams. As it contained some green colouring matter, it was first treated with alcohol, and subsequently recrystallised several times from dilute pyridine, when it was obtained in minute, colourless crystals, melting and decomposing at 295—300°. It yielded colour reactions similar to those given by the phytosterols:

0.1014 gave 0.2662 CO₂ and 0.0948 H₂O. C=71.6; H=10.4.

C₂₁H₃₆O₄ requires C=71.6; H=10.2 per cent.

A determination of its optical rotatory power gave the following result:

0.2944, made up to 20 c.c. with pyridine, gave $\alpha_D - 1^\circ 18'$ in a 2-dcm. tube, whence $[\alpha]_D - 44.1^\circ$.

An acetyl derivative of the substance was prepared, and this, when crystallised from a mixture of ethyl acetate and alcohol, separated in flat needles, melting at 165—166°. It was analysed, and its optical rotatory power determined, with the following results:

0.1208 gave 0.3038 CO₂ and 0.0996 H₂O. C=68.6; H=9.2.

C₂₁H₃₄O₂(CO·CH₃)₂ requires C=68.8; H=9.2 per cent.

0.3122, made up to 20 c.c. with chloroform, gave $\alpha_D - 0^\circ 49'$ in a 2-dcm. tube, whence $[\alpha]_D - 26.1^\circ$.

These results render it evident that the above-described substance is identical with trifolanol (compare Power and Salway, this vol., p. 249).

The ethereal solution of the ethereal extract from which the trifolanol had been separated was evaporated, when 12 grams of a dark green resin were obtained. This was of an acidic nature, but yielded nothing of interest.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

These extracts were dark-coloured resins, amounting to 5, 2·5, and 8·3 grams respectively. They were thoroughly examined, but nothing definite could be isolated from them.

Summary.

The results of this investigation may be briefly summarised as follows:

The material employed consisted of the dried flowering tops of the carnation clover (*Trifolium incarnatum*, Linné). An alcoholic extract of this material, when distilled with steam, yielded an essential oil in an amount equivalent to 0·029 per cent. of the dried flowers. This essential oil, which contained furfuraldehyde, possessed a strong persistent odour, and the following constants: $d_{20^{\circ}/20^{\circ}} = 0\cdot9597$; $\alpha_D - 1^{\circ}48'$ in a 1-dm. tube.

The portion of the alcoholic extract which was soluble in water contained a considerable quantity of a sugar which yielded *d*-phenyl-glucosazone (m. p. 205—206°), and from the aqueous liquid the following definite substances were isolated: benzoic and salicylic acids, in very small amount, with apparently a trace of *p*-coumaric acid; pratol, $C_{16}H_{12}O_4$; quercetin, $C_{15}H_{10}O_7$, and a new glucoside of the latter, $C_{21}H_{20}O_{12}\cdot 3H_2O$ (m. p. 242—245°), which has been designated *incarnatrin*.

The portion of the alcoholic extract which was insoluble in water consisted chiefly of green, resinous material, the amount of which was equivalent to 4·1 per cent. of the weight of the dried flowers. From this resin the following compounds were obtained: an alcohol, $C_{34}H_{69}\cdot OH$ (m. p. 72—74°), which had previously been obtained from the wax of the humble-bee, and which it is now proposed to designate *incarnatyl alcohol*; hentriacontane, $C_{31}H_{64}$; a phytosterol, $C_{27}H_{46}O$ (m. p. 135—136°; $[\alpha]_D - 41\cdot7^{\circ}$), which yields an acetyl derivative melting at 124—125°, and having $[\alpha]_D - 43\cdot9^{\circ}$; trifolianol, $C_{21}H_{34}O_2(OH)_2$ (m. p. 295—300°; $[\alpha]_D - 44\cdot1^{\circ}$), and a mixture of fatty acids, consisting chiefly of palmitic, stearic, and linolic acids, with smaller amounts of oleic and *isolinolenic* acids.

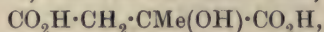
In conclusion, the author wishes to express his indebtedness to Dr. F. B. Power for having suggested this research, and for the kind interest he has shown throughout the course of the work.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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LXXX.—*Experiments on the Walden Inversion. Part IV.*
The Interconversion of the Optically Active
Phenylmethylglycollic Acids.

By ALEX. McKENZIE and GEORGE WILLIAM CLOUGH.

THE carboxylic acids which have so far been investigated from the point of view of the Walden inversion contain a hydrogen atom in direct attachment to an asymmetric carbon atom. Work has not been conducted with compounds which do not contain a hydrogen atom directly linked to asymmetric carbon because the number of known optically active hydroxy-acids of this class is very limited. Marckwald and Axelrod (*Ber.*, 1899, **32**, 712) oxidised optically active valeric acid to the corresponding hydroxy-acid, namely, α -hydroxy- α -methylbutyric acid, in the hope of obtaining the latter compound in an active form, but complete racemisation occurred. The same authors have, however, resolved citramalic acid,



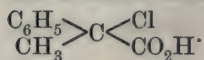
into its optically active components, and point out that an examination of this compound, where the presumably less labile methyl group has taken the place of a hydrogen atom in malic acid, might be of interest when viewed in relationship with Walden's interconversion of the malic acids. Marckwald and Axelrod have not, however, prosecuted the study of citramalic acid in this direction.

In the course of work on asymmetric synthesis, one of us has had to deal repeatedly with mixtures of unequal amounts of *d*- and *l*-phenylmethylglycollic acids (*Trans.*, 1904, **85**, 1249, and subsequent papers). The most pronounced asymmetric synthesis of phenylmethylglycollic acid accomplished by aid of the Grignard action gave an acid mixture with $[\alpha]_D - 9.5^\circ$ in ethyl-alcoholic solution, but the extent of this synthesis could not at the time be estimated, since the specific rotatory power of the active phenylmethylglycollic acids was not known. It was accordingly desirable to carry out the resolution of *r*-phenylmethylglycollic acid, and the results obtained are now recorded in the present communication.

The resolution is effected in water solution by the aid of morphine, the alkaloidal salt of the *l*-acid being more sparingly soluble than that of the *d*-isomeride. Quinine may also be used in ethyl-alcoholic solution, and in this case the quinine salt of the *d*-acid is the more sparingly soluble of the two diastereoisomerides. The active acids prepared in this manner have $[\alpha]_D \pm 37.7^\circ$ in ethyl-alcoholic solution.

Since phenylmethylglycollic acid, $\text{C}_6\text{H}_5 > \text{C} \begin{matrix} \text{OH} \\ \text{CO}_2\text{H} \end{matrix}$, does not contain a hydrogen atom directly attached to the asymmetric carbon atom, it

was decided to find out if the active acids were interconvertible by the Walden inversion through the α -chloro- α -phenylpropionic acids,



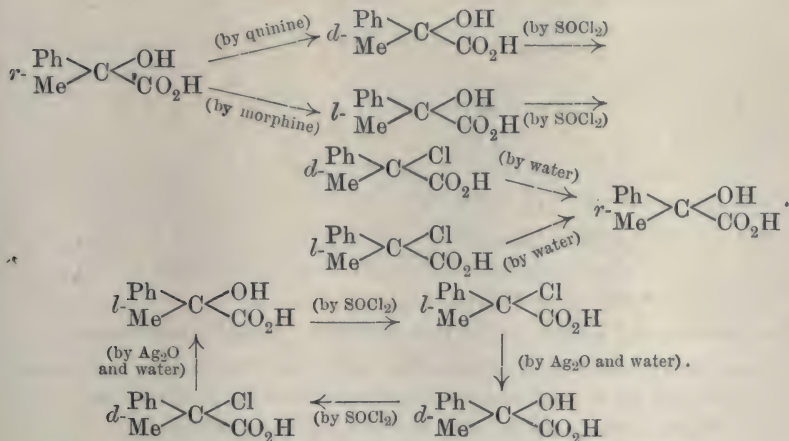
When *l*-phenylmethylglycollic acid is treated at the ordinary temperature with fuming hydrochloric acid, it is converted into *r*- α -chloro- α -phenylpropionic acid, complete racemisation taking place in this change.

Attempts to resolve *r*- α -chloro- α -phenylpropionic acid into its active isomerides held out little hope of success, owing partly to the extreme facility with which the chlorine atom is displaced by the hydroxy-group. The active chloro-acids were, however, obtained by the action of thionyl chloride at the ordinary temperature on the corresponding active phenylmethylglycollic acids. There is no change of sign of rotation in this conversion, *l*-phenylmethylglycollic acid passing into *l*- α -chloro- α -phenylpropionic acid, with $[\alpha]_D - 26.0^\circ$ in benzene solution.

When *l*- α -chloro- α -phenylpropionic acid is dissolved in water, it is converted with great ease at the ordinary temperature into *r*-phenylmethylglycollic acid, the racemisation being complete. The action of aqueous sodium hydroxide is similar.

A change of sign takes place, however, when a mixture of the *l*-chloro-acid, silver oxide, and water is shaken at the ordinary temperature. The resulting phenylmethylglycollic acid had $[\alpha]_D + 9.4^\circ$ in ethyl-alcoholic solution, so that partial racemisation had taken place in this change. One is concerned here with at least two distinct actions, namely, action of water on the *l*-chloro-acid, and action of water and silver oxide on the *l*-acid. The racemisation observed is mainly, if not entirely, due to the first of these actions.

The following changes have been effected :



EXPERIMENTAL.

Resolution of r-Phenylmethylglycollic Acid into its Optically Active Components.

Thirty-seven grams of *r*-phenylmethylglycollic acid (1 mol.), prepared from acetophenone and hydrogen cyanide by modifying Spiegel's method (*Ber.*, 1881, **14**, 1353), were dissolved in 2300 c.c. of boiling water, and 64 grams of powdered morphine (1 mol.) were gradually added. The alkaloid dissolved with ease, and the boiling was continued for a few minutes until the solution was clear. On cooling, glassy prisms grouped in rosettes began to separate. The solution, when still warm, was placed in an ice-chest at 10°, and 44 grams of salt had separated on the following day. After five more crystallisations from water, 19 grams of the pure morphine salt of the *l*-acid were obtained. The progress of the resolution was tested by removing the morphine from successive filtrates, and polarimetrically examining the resulting acid in ethyl-alcoholic solution, this method being preferred to the customary one of examining successive crops of the alkaloidal salt. The last four filtrates gave acids with the values $[\alpha]_D -20.9^\circ$, -33° , -36.2° , and -37.9° respectively. When the 19 grams of salt were again crystallised, the filtrate gave an acid with $[\alpha]_D -37.9^\circ$. The *l*-acid was then obtained from the homogeneous morphine salt by acidification with sulphuric acid and extraction with ether.

It appeared from another experiment, where 44 grams of *r*-phenylmethylglycollic acid were employed, that the resolution is fairly complete, even after two crystallisations, under conditions similar to the above. The resulting acid was crystallised once from benzene, and then amounted to 14 grams, with $[\alpha]_D -35^\circ$ in ethyl-alcoholic solution.

l-Phenylmethylglycollic acid, $\text{OH} \cdot \text{CMePh} \cdot \text{CO}_2\text{H}$, dissolves readily in ethyl alcohol or acetone. It is easily soluble in hot benzene, but sparingly soluble in the cold solvent, from which it separates in silky needles, m. p. 116—117°. It may also be crystallised from water, in which it is more soluble than is the *r*-isomeride. It differs from the *r*-acid (m. p. 93—94°) in being devoid of water of crystallisation:

0.1360 gave 0.3232 CO_2 and 0.0736 H_2O . $\text{C} = 64.8$; $\text{H} = 6.1$.

$\text{C}_9\text{H}_{10}\text{O}_3$ requires $\text{C} = 65.0$; $\text{H} = 6.1$ per cent.

Analysis of the *silver* salt gave:

Found: $\text{Ag} = 39.4$. $\text{C}_9\text{H}_9\text{O}_3\text{Ag}$ requires $\text{Ag} = 39.5$ per cent.

The purity of the acid was further controlled by finding that, when it is crystallised several times either from benzene or from water, the value for the specific rotation of the product is not altered.

The following polarimetric observations were made.

In ethyl-alcoholic solution :

$$l = 2, c = 3.354, \alpha_D^{13.8} - 2.53^\circ, [\alpha]_D^{13.8} - 37.7^\circ.$$

In acetone solution :

$$l = 2, c = 4.142, \alpha_D^{13} - 3.02^\circ, [\alpha]_D^{13} - 36.5^\circ.$$

In aqueous solution :

$$l = 2, c = 2.160, \alpha_D^{14.5} - 2.21^\circ, [\alpha]_D^{14.5} - 51.1^\circ.$$

$$l = 4, c = 1.5892, \alpha_D^{13} - 3.34^\circ, [\alpha]_D^{13} - 52.5^\circ.$$

$$l = 2, c = 0.688, \alpha_D^{14.5} - 0.74^\circ, [\alpha]_D^{14.5} - 53.8^\circ.$$

The specific rotation of the acid in aqueous solution increases with dilution. An aqueous solution of the sodium salt should, therefore, give a value higher than any of the three preceding values, and this is the case. The following observations were made with an aqueous solution of sodium salt :

$$l = 2, c = 1.920, \alpha_D^{13.5} - 2.17^\circ, [\alpha]_D^{13.5} - 56.5^\circ.$$

$$l = 2, c = 4.916, \alpha_D^{14.7} - 5.60^\circ, [\alpha]_D^{14.7} - 57.0^\circ.$$

It is not unimportant to note that the polarimetric observations with the free acid were made with samples which had previously been dried under diminished pressure at the ordinary temperature over sulphuric acid. The active acid should not be dried at 100° , since water is slowly eliminated from it at this temperature with the consequent formation of atropic acid.

The first two mother liquors from the morphine resolution quoted gave a dextrorotatory acid mixture (22 grams) with $[\alpha]_D + 19.4^\circ$ in ethyl-alcoholic solution. This acid was dissolved in 550 c.c. of boiling ethyl alcohol, and neutralised by 47 grams of quinine. Forty grams of quinine salt separated, and the acid obtained from it had $[\alpha]_D + 28.3^\circ$ in ethyl-alcoholic solution. Owing to the greater solubility of the active as compared with the *r*-acid, it is not practical to separate the *d*-acid from this mixture by crystallisation. After two crystallisations from water, the acid was in fact less active than before, having $[\alpha]_D + 26^\circ$ in ethyl-alcoholic solution.

For the preparation of the *d*-acid, 64 grams of quinine (1 mol.) were dissolved in 700 c.c. of boiling ethyl alcohol, and 30 grams of *r*-phenyl-methylglycollic acid (1 mol.) were added. After fifty minutes, crystallisation started, and the solution was then placed in an ice-chest at 10° . The resulting crystals, which contain a preponderance of the quinine salt of the *d*-acid, were withdrawn next day, and repeatedly crystallised from the minimum amount of boiling ethyl alcohol. The resolution proceeds rather more slowly than when morphine was used, the progress being tested by decomposing the mother liquors as before. After four crystallisations, the salt amounted to 19 grams, but was not

quite pure, the acid obtained from a portion of it having $[\alpha]_D + 34.6^\circ$ in ethyl-alcoholic solution. After three additional crystallisations, the salt, which separated in glassy needles, grouped in rosettes, was pure, and amounted to 11 grams; it melts and decomposes at about 216° . The *d*-acid was obtained from it by acidification and extraction with ether.

d-Phenylmethylglycollic acid melts at $116\text{--}117^\circ$, and in other respects resembles the *l*-isomeride:

0.1558 gave 0.3712 CO_2 and 0.0865 H_2O . $\text{C} = 65.0$; $\text{H} = 6.2$.

$\text{C}_9\text{H}_{10}\text{O}_3$ requires $\text{C} = 65.0$; $\text{H} = 6.1$ per cent.

Its specific rotation was determined in ethyl-alcoholic solution:

$l = 4$, $c = 3.500$, $\alpha_D^{10.5} + 5.27^\circ$, $[\alpha]_D^{10.5} + 37.7^\circ$.

Conversion of l-Phenylmethylglycollic Acid into r- α -Chloro- α -phenylpropionic Acid.

l-Phenylmethylglycollic acid (3 grams) was added to 100 c.c. of aqueous hydrochloric acid ($D\ 1.2$). The mixture was shaken occasionally during four hours, by which time the acid had dissolved. Next day, the lustrous plates (1.9 grams), which had separated, were dissolved in benzene and found to be optically inactive, and to consist of *r- α* -chloro- α -phenylpropionic acid, melting at $75\text{--}76^\circ$. The filtrate was gradually evaporated to dryness at the ordinary temperature over soda-lime for five months; the resulting crystals were optically inactive when examined polarimetrically in ethyl-alcoholic solution.

Optically Active α -Chloro- α -phenylpropionic Acids.

The first attempts to obtain these acids were made by combining *r- α* -chloro- α -phenylpropionic acid with various alkaloids, but it soon appeared that the chlorine is so readily removed from this acid as to render the complete resolution a difficult task. *r- α* -Chloro- α -phenylpropionic acid in the presence of water was found to pass with great ease into *r*-phenylmethylglycollic acid even at the ordinary temperature, and when a methyl-alcoholic solution of the chloro-acid is neutralised by heating with morphine or with cinchonine, the hydrochloride of the alkaloid separates. A partial resolution is, however, effected when a methyl-alcoholic solution of the *r*-acid is neutralised by morphine at the ordinary temperature; the salt which separates under certain conditions gives a dextrorotatory chloro-acid, whilst, under other conditions, a levorotatory acid mixture can be obtained, this behaviour recalling the phenomena observed during the resolution of *r*-phenylchloroacetic acid by morphine (Trans., 1909, 95, 777). Owing to the insolubility of the morphine salt in various organic solvents, the usual method of conducting a resolution was not employed. By half

neutralising a methyl-alcoholic solution of the *r*-acid with morphine at the ordinary temperature, obtaining the acid from the resulting crystals, and then repeating this treatment, an acid was obtained with $[\alpha]_D - 16.3^\circ$ in benzene solution, but it was clear that the product was not homogeneous.

The action of thionyl chloride on *r*-phenylmethylglycollic acid was then examined. By gradually heating the acid to 100° with an excess of thionyl chloride, *dl*- α -chloro- α -phenylpropionyl chloride was obtained as an oil, b. p. $108^\circ/15$ mm. :

Found : Cl = 34.8. $C_9H_9OCl_2$ requires Cl = 34.9 per cent.

r- α -Chloro- α -phenylpropionic acid is readily obtained from the acid chloride by means of aqueous acetone.

The conversion into the chloro-acid can, however, be brought about directly by the action of thionyl chloride on *r*-phenylmethylglycollic acid even at the ordinary temperature. Fortunately, when the action is applied to the optically active phenylmethylglycollic acids, the extent of the racemisation is so slight as to render possible the preparation of the active chloro-acids.

A mixture of *d*-phenylmethylglycollic acid (10 grams) and thionyl chloride (28 grams) was kept at the ordinary temperature for twenty-four hours. The excess of thionyl chloride was then removed from the red liquid under diminished pressure over sodium hydroxide at the ordinary temperature. After draining on porous plate, the resulting solid (5 grams) was crystallised twice from light petroleum, after which it was found that the value for its specific rotation did not alter on further crystallisation.

d- α -Chloro- α -phenylpropionic acid, $CMePhCl \cdot CO_2H$, separates from light petroleum in colourless, glassy prisms and melts at $70-72^\circ$, whereas the inactive acid melts at $75-76^\circ$:

Found : Cl = 19.0. $C_9H_9O_2Cl$ requires Cl = 19.3 per cent.

Its specific rotation was determined in benzene solution :

$l = 2$, $c = 1.690$, $\alpha_D^{15} + 0.88^\circ$, $[\alpha]_D^{15} + 26.0^\circ$.

The acid is very readily soluble in ethyl alcohol, ether, or benzene.

l- α -Chloro- α -phenylpropionic acid, prepared from *l*-phenylmethylglycollic acid in a similar manner, melts at $70-72^\circ$, and in other respects resembles its enantiomorphously related isomeride :

Found : Cl = 19.4. $C_9H_9O_2Cl$ requires Cl = 19.3 per cent.

Its specific rotation was determined in benzene solution :

$l = 2$, $c = 2.268$, $\alpha_D^{14} - 1.18^\circ$, $[\alpha]_D^{14} - 26.0^\circ$.

Conversion of d- and l- α -Chloro- α -phenylpropionic Acids into r-Phenylmethylglycollic Acid.

It was shown by titration with standard alkali that, when *r*- α -chloro- α -phenylpropionic acid (1 gram) is dissolved in cold water (100 c.c.), the chlorine is so readily displaced by the hydroxy-group that the complete conversion into phenylmethylglycollic acid takes place almost as quickly as the chloro-acid dissolves. The behaviour of the active chloro-acids is of course similar to this.

l- α -Chloro- α -phenylpropionic acid (1 gram) was shaken with 25 c.c. of water for twenty minutes. The solution was then only slightly lævorotatory, and *r*-phenylmethylglycollic acid began to separate. After heating for ten minutes, the acid was removed from the solution by extraction with ether; it was free from chlorine and quite inactive.

The *d*-chloro-acid was also converted into *r*-phenylmethylglycollic acid by the action of water; the same result was also obtained by the action of aqueous sodium hydroxide in an amount which corresponded with that necessary for neutralisation of the carboxyl group and displacement of halogen.

It was shown in a former paper that a dextrorotatory mixture of phenylaminoacetic acids is formed by the action of ammonia on *l*-phenylchloroacetic acid, whilst, at the same time, the action of water and excess of ammonia on ammonium *l*-phenylchloroacetate gives rise to a mandelic acid mixture of fairly high activity. When, however, *l*- α -chloro- α -phenylpropionic acid (1 gram) was dissolved in 25 c.c. of ammonia (*D* 0.88), the resulting atrolactic acid was inactive.

Action of Silver Oxide and Water on d- and l- α -Chloro- α -phenylpropionic Acids.

Silver oxide, prepared from 1 gram of nitrate, was added to 25 c.c. of water, and 1 gram of the *l*-chloro-acid was then added. Silver chloride began to form at once, and, after shaking for thirty minutes, the mixture was kept at the ordinary temperature for two hours. After heating at 100° for ten minutes, dilute hydrochloric acid was added, and the phenylmethylglycollic acid was isolated from the filtrate. The mixture of phenylmethylglycollic acids obtained in this manner was free from chlorine, melted at 80—89°, and was dextrorotatory. In ethyl-alcoholic solution:

$$l = 2, c = 5.46, \alpha_D + 1.03^\circ, [\alpha]_D + 9.4^\circ.$$

A similar result was obtained when the *l*-chloro-acid was added to an aqueous solution of silver nitrate.

d- α -Chloro- α -phenylpropionic acid (1 gram) was added to 10 c.c. of water, in which silver oxide, prepared from 1 gram of nitrate, was suspended. After shaking for thirty minutes at the ordinary temperature, dilute hydrochloric acid was added, and the filtrate evaporated to 25 c.c. The solution was lævorotatory, giving $\alpha_D - 0.85^\circ$ in a 4-dem. tube. The phenylmethylglycollic acid extracted from it was free from chlorine, melted at $81-90^\circ$, and gave the following value in ethyl-alcoholic solution:

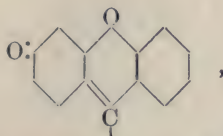
$$l = 2, c = 3.01, \alpha_D - 0.50^\circ, [\alpha]_D - 8.3^\circ.$$

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LXXXI.—*Fluorones.*

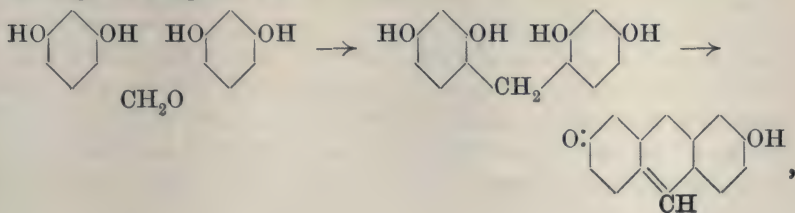
By FRANK GEORGE POPE and HUBERT HOWARD.

So far as we can ascertain, the first use of the term fluorone to describe a certain type of heterocyclic compound was made by Möhlau and Koch (*Ber.*, 1894, **27**, 2887), who designated as "fluorone" the following complex:

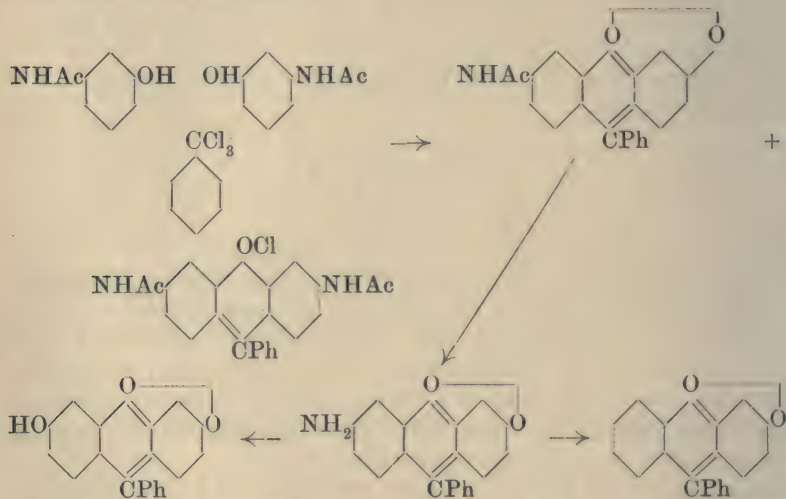


and, since they obtained compounds of this type by the condensation of phenols with aldehydes, the aldehydic grouping appearing in the pyrone ring of the complex, named their compounds according to the aldehyde used as formaldehydefluorone, etc. Kehrmann, however, in 1908, considering the group as a whole, gave to the parent substance the name fluorone, and considered all substances derived from it without reference to the particular aldehyde used.

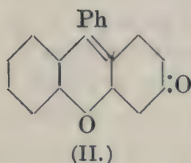
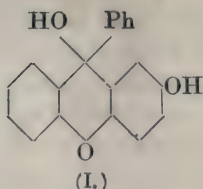
The fluorones of Möhlau and Koch were obtained by the condensation of two molecules of resorcinol with one molecule of an aliphatic aldehyde in the presence of dilute (1 : 5) sulphuric acid, the resulting diphenylmethane derivative being then oxidised to the fluorone by heating with sulphuric acid:



and from their mode of formation they were considered to be compounds of a para-quinonoid type. The hydroxyfluorones obtained in this way were readily soluble in solutions of the alkaline hydroxides, such solutions showing a marked fluorescence. In a similar manner, Weidel and Wenzel (*Monatsh.*, 1900, **21**, 62), Schreier and Wenzel (*ibid.*, 1904, **25**, 311), Liebermann and Lindenbaum (*Ber.*, 1904, **27**, 1171, 2728), by using substituted phloroglucinols and hydroxyquinols in the presence of hydroxyaldehydes, have also prepared many fluorone derivatives. Kehrman (*Ber.*, 1908, **41**, 3440) has obtained phenylfluorone and hydroxyphenylfluorone, starting from acetyl-*m*-aminophenol and benzotrichloride, which, when heated together in nitrobenzene solution at 160°, yield diacetylrosamine chloride and acetylaminophenylfluorone. The acetylaminophenylfluorone is then hydrolysed and the amino-group diazotised, when hydroxyphenylfluorone or phenylfluorone is obtained, accordingly as the diazo-solution is boiled alone or with alcohol, thus :

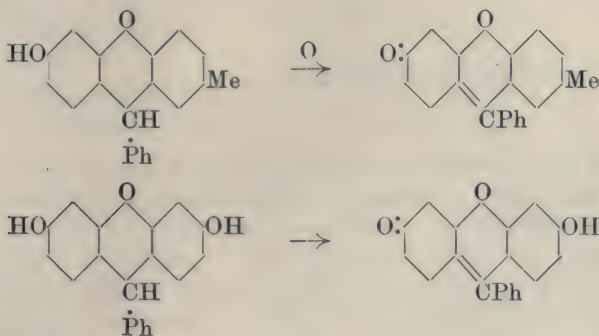


and, in accordance with his well-known views, Kehrman ascribes to these compounds the betaine type of orthoquinonoid structure. This view is combated by Decker (*Ber.*, 1909, **42**, 578), who has tried to prepare the analogue of phenylfluorone from quinolphthalein by hydrolysis of 2-methoxy-9-phenylxanthonium bromide and subsequent neutralisation, but the only product obtained was a colourless carbinol base, namely, 2-hydroxy-9-phenylxanthen-9-ol (I), which shows that there is a fundamental difference between the two series, and the conclusion is drawn that phenylfluorone (II) must have a para-quinonoid structure :



Again, Decker also found that 3-methoxy-9-phenylxanthonium chloride, when heated with hydrochloric acid under pressure, yielded the corresponding hydroxy-compound, which was converted by sodium hydroxide into phenylfluorone, the properties of which bear no resemblance to those of a phenol-betaine, which should be soluble in water.

In the course of this investigation, we have found that the hydroxy-xanthenes obtained by the condensation of dihydroxybenzhydrols with phenols may be oxidised quite readily to fluorones by drawing a slow current of air through their solutions in the alkaline hydroxides, and in this way we have prepared phenylmethylfluorone and 3-hydroxy-9-phenylfluorone, thus:



and it seems to us that since the above phenylmethylfluorone is insoluble in water and also is quite insoluble in solutions of sodium hydroxide, even when boiled, that the betaine formula of Kehrman is untenable, and the compounds in question must be considered as para-quinonoid in structure.

Kehrman is also of the opinion that hydroxyphenylfluorone is identical with Doebner's resorcinolbenzein, $C_{38}H_{30}O_9$, a view which has been denied by H. v. Liebig (*J. pr. Chem.*, 1908, [ii], 78, 534). We are inclined to support Kehrman's views in this matter from a few experiments we have made with resorcinolbenzein as prepared by Cohn from the condensation of resorcinol with benzoic acid in the presence of zinc chloride. A consideration of the formula given by Doebner might suggest that resorcinolbenzein was a hydrated form of hydroxy-phenylfluorone, $2(C_{19}H_{12}O_3) \cdot 3H_2O$. We found that Cohn's preparation

gave varying numbers on analysis, and in order to see that the preparation was quite dry, it was heated for many hours at 200° , when it became quite solid after having previously melted at about 150° . Analysis of this product showed a considerable increase in the percentage of carbon, approaching to the value for that of the fluorone. The compound was then heated under reflux with nitrobenzene for some hours, and the solution filtered into light petroleum, when a dark brown, flocculent precipitate was obtained, which was collected, well washed with light petroleum, and dried until quite free from all traces of nitrobenzene:

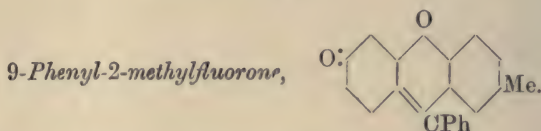
0.0504 gave 0.1445 CO_2 and 0.0158 H_2O . $\text{C} = 78.19$; $\text{H} = 3.48$.

$\text{C}_{38}\text{H}_{30}\text{O}_9$ requires $\text{C} = 72.38$; $\text{H} = 4.76$ per cent.

$\text{C}_{19}\text{H}_{12}\text{O}_3$ „ $\text{C} = 79.16$; $\text{H} = 4.16$ „

On these grounds we think that Kehrmann's views are correct, but we hope to return to the subject shortly, since we think that many of the products obtained from resorcinolbenzein can be explained on the same grounds.

EXPERIMENTAL.

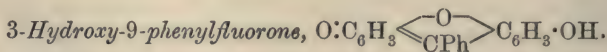


Two grams of 6-hydroxy-9-phenyl-2-methylxanthen were dissolved in an excess of dilute sodium hydroxide solution, and a stream of air was drawn through the liquid for several days. The colour of the solution was gradually discharged until it became of a faint brown shade, and a dark-coloured solid gradually separated. This was collected, washed, dried, and recrystallised from absolute alcohol:

0.1156 gave 0.3550 CO_2 and 0.0520 H_2O . $\text{C} = 83.75$; $\text{H} = 4.99$.

$\text{C}_{20}\text{H}_{14}\text{O}_2$ requires $\text{C} = 83.91$; $\text{H} = 4.89$ per cent.

9-Phenyl-2-methylfluorone is an orange-red, crystalline powder, which is only very sparingly soluble in alcohol or chloroform. It is quite insoluble in aqueous alkali hydroxides, and even in dilute solutions of the mineral acids. It dissolves in concentrated sulphuric acid to a dark reddish-brown solution, from which it is reprecipitated by the addition of water. It melts at 201° .



Five grams of 3:6-dihydroxy-9-phenylxanthen were dissolved in an excess of *N*-sodium hydroxide solution, and a stream of air was drawn through the solution for two or three days. The dark-

coloured solution was then diluted with water and acidified with dilute hydrochloric acid, when a dark brown finely-divided precipitate was obtained. This was collected, well washed, and dried, and finally recrystallised from alcohol, from which it separates in dark brown scales possessing a deep blue reflex:

0.1180 gave 0.3418 CO_2 and 0.0436 H_2O . $\text{C} = 79.00$; $\text{H} = 4.10$.

$\text{C}_{19}\text{H}_{12}\text{O}_3$ requires $\text{C} = 79.17$; $\text{H} = 4.17$ per cent.

3-Hydroxy-9-phenylfluorone is a dark brown powder, which is readily soluble in alkali hydroxides, the solution obtained showing a strong green fluorescence. It is soluble in concentrated sulphuric acid, with formation of a brown solution. Since analysis is not quite sufficient to determine the difference between the hydroxyfluorone and the corresponding xanthen, which requires $\text{C} = 78.62$; $\text{H} = 4.83$ per cent., the fluorone was acetylated by heating it with five times its weight of acetic anhydride and its own weight of fused sodium acetate for three hours under reflux. The product was poured into dilute alcohol and warmed on the water-bath for some time in order to remove the excess of anhydride. It was then collected, washed, and dried. For analysis it was dissolved in chloroform and precipitated by light petroleum:

0.1015 gave 0.2836 CO_2 and 0.0390 H_2O . $\text{C} = 76.20$; $\text{H} = 4.27$.

$\text{C}_{21}\text{H}_{14}\text{O}_4$ requires $\text{C} = 76.31$; $\text{H} = 4.27$ per cent.,

whereas the dihydroxyxanthen diacetate requires $\text{C} = 73.80$; $\text{H} = 4.81$ per cent. Thus there seems to be no doubt that the original compound is the fluorone. *3-Acetoxy-9-phenylfluorone* is a dark brown-coloured powder.

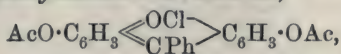
Attempts were made to prepare a hydroxyphenylfluorone hydrochloride, but the product obtained did not give sharp numbers on analysis. The method adopted for the preparation was to dissolve the fluorone in chloroform and saturate the solution with hydrogen chloride, when a dark reddish-brown precipitate was produced. We then modified the method by weighing out a definite quantity in a porcelain boat, which was placed in a piece of glass tubing, and a slow stream of hydrogen chloride was passed over it for several hours and the gain in weight noted:

0.1132 gave 0.1286 hydrochloride.

The ratio $\text{C}_{19}\text{H}_{12}\text{O}_3 \cdot \text{HCl} : \text{C}_{19}\text{H}_{12}\text{O}_3 = 1.127 : 1$.

Actual ratio obtained = 1.136.

3 : 6-Diacetoxy-9-phenylxanthonium chloride,



was prepared by dissolving 2.88 grams of 3-hydroxy-9-phenylfluorone in

chloroform and stirring into the solution 1.57 grams of acetyl chloride. The dark brown precipitate was collected and well washed with chloroform and benzene, and then dried:

0.1162 gave 0.2896 CO_2 and 0.0482 H_2O . $\text{C} = 67.97$; $\text{H} = 4.60$.

$\text{C}_{23}\text{H}_{17}\text{O}_5\text{Cl}$ requires $\text{C} = 67.56$; $\text{H} = 4.16$ per cent.

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LXXXII.—*The Resin Acids of the Coniferae.* Part II.* *Matairesinol.*

By THOMAS HILL EASTERFIELD and JAMES BEE.

THE Matai (*Podocarpus spicatus*) is a handsome tree which occurs freely in the forests of the North and South Island of New Zealand. The timber is valued on account of its straight grain and durability. The heart wood often exhibits shakes or cracks, which are generally lined with a yellowish-white deposit, sometimes amorphous, but often containing groups of radiating crystals.

It seemed probable that this crystalline material would be found to consist of podocarpic acid, which forms the greater part of the heart resin of *Podocarpus cupressinum* (Oudemans, *Annalen*, 1873, 170, 213). When, however, the resin was treated with alcohol, in which podocarpic acid dissolves easily, it was found to be but sparingly soluble. After crystallisation from hot alcohol and subsequently from 70 per cent. acetic acid, the substance was found to have the formula $\text{C}_{19}\text{H}_{20}\text{O}_6$; it is thus isomeric with pinoresinol discovered by M. Bamberger (*Monatsh.*, 1897, 18, 481) in the exudation resins of *Pinus laricio* and *Picea vulgaris*. The name "*matairesinol*" is therefore given to the new compound.

Matairesinol resembles pinoresinol in that two of the six oxygen atoms occur as hydroxy- and two as methoxy-groups; the third pair of oxygen atoms in matairesinol is lactonic, whilst in pinoresinol the nature of the third pair has not yet been determined. The most striking difference between the two compounds, is that, whereas pinoresinol forms a sparingly soluble potassium salt, the corresponding salt of matairesinol is exceedingly soluble both in water and in alcohol.

* In Part I. of this series (*Trans.*, 1904, 85, 1238) it was suggested as not improbable that the resin acids as a class would be found to be hydrogenised phenanthrene derivatives. Prof. Tschirsch has drawn my attention to the fact that he had previously put forward a "three-ring" hypothesis. I regret that Prof. Tschirsch's papers had escaped my notice.—T. H. E.

EXPERIMENTAL.

Preparation of Matairesinol.

The yellowish-white mixture of crystalline and amorphous material scraped from the lining of the heart cracks of the matai timber was boiled with methylated spirit, filtered, and allowed to crystallise, the spirit being then used again for treating a fresh portion of the sparingly soluble resin. By a single recrystallisation from alcohol, the substance was obtained in almost colourless needles melting at 77—78°; further recrystallisation did not alter the melting point. Thus obtained, the compound contains alcohol of crystallisation, which it slowly loses if kept over sulphuric acid in a vacuum desiccator. Two preparations were analysed :

0.847 lost 0.094 C_2H_6O at 50° and 21 mm. $C_2H_6O = 11.1$.

0.2652 gave 0.6256 CO_2 and 0.1524 H_2O . $C = 64.4$; $H = 6.4$.

0.2050 „ 0.4838 CO_2 „ 0.1252 H_2O . $C = 64.4$; $H = 6.8$.

$C_{19}H_{20}O_6 \cdot C_2H_6O$ requires $C_2H_6O = 11.8$; $C = 64.6$; $H = 6.6$ per cent.

After expelling the alcohol of crystallisation, the compound melted at 119°; the same melting point was observed with specimens crystallised from slightly dilute acetic acid and from acetone. Preparations obtained by these three methods gave the following data :

0.2194 gave 0.5326 CO_2 and 0.1182 H_2O . $C = 66.2$; $H = 6.0$.

0.2018 „ 0.4914 CO_2 „ 0.1054 H_2O . $C = 66.4$; $H = 5.8$.

0.2580 „ 0.6282 CO_2 „ 0.1366 H_2O . $C = 66.4$; $H = 5.8$.

$C_{19}H_{20}O_6$ requires $C = 66.3$; $H = 5.8$ per cent.

Molecular-weight determinations :

0.2322 in 12.6 of phenol gave $\Delta^t - 0.40^\circ$. M.W. = 331.

0.472 „ 6 „ alcohol „ $E + 0.28^\circ$. M.W. = 328.

0.2472 neutralised 3.6 c.c. $N/5$ -NaOH. M.W. = 343.

0.1558 „ 2.3 c.c. $N/5$ -NaOH. M.W. = 345.

$C_{19}H_{20}O_6$ requires M.W. = 344.

The specific rotation was determined in acetone solution at concentrations of 22 grams, 10 grams, and 5 grams per 100 c.c. of solution; in each case the value $[\alpha]_D^{25} - 4.89^\circ$ was obtained.

The following approximate solubilities were observed (grams per 100 grams of solvent): Acetone (12°) 179; chloroform (12°) 35; ethyl acetate (12°) 27; methyl alcohol (12°) 16.7; ethyl alcohol (18°) 9; amyl alcohol (12°) 4.6; toluene (12°) 1.9; ether (12°) 0.8; benzene (12°) 0.3; water (100°) 0.19; water (20°) 0.02; in light petroleum the compound is not appreciably soluble.

The alcoholic solution of matairesinol is neutral to phenolphthalein; when warmed with excess of alkali and neutralised with standard acid,

a molecule of alkali is found to have combined with a molecule of the substance. Sodium hydroxide dissolves the compound in the cold, but hot sodium carbonate only dissolves it slowly. Mineral acids reprecipitate the original compound, but acetic acid throws out a hydroxy-acid, which is described below. Matairesinol is thus undoubtedly a lactone.

Matairesinol crystallises from 60 per cent. acetic acid in large prisms. When melted and allowed to cool, it sets to a transparent glass, which shows no tendency to crystallise unless brought into contact with some liquid in which it is slightly soluble. The alcoholic solution gives a deep green colour with an aqueous solution of ferric chloride.

The compound cannot be distilled even under a pressure of 20 mm. without decomposition; the distillate has an odour both of guaiacol and eugenol.

Determination of Methoxy-groups.—Perkin's modification of Zeisel's method was employed:

0.2496 gave 0.3206 AgI. OMe = 17.0.

0.2490 „ 0.3262 AgI. OMe = 17.4.

$C_{17}H_{14}O_4(OMe)_2$ requires OMe = 18 per cent.

Monoacetylmatairesinol was prepared by boiling with excess of acetyl chloride, washing the sticky product with water, and crystallising from dilute alcohol; it formed colourless needles, which melted at 110° :

0.2150 gave 0.5154 CO_2 and 0.1120 H_2O . C = 65.4; H = 5.8.

$C_{21}H_{22}O_7$ requires C = 65.3; H = 5.7 per cent.

[The diacetyl derivative requires C = 64.5; H = 5.6 per cent.]

Dibenzoylmatairesinol was prepared from the sodium hydroxide solution and benzoyl chloride; when recrystallised from alcohol it melted at 133° . Two preparations gave:

0.2224 gave 0.5842 CO_2 and 0.1032 H_2O . C = 71.6; H = 5.1.

0.1720 „ 0.4526 CO_2 „ 0.0778 H_2O . C = 71.8; H = 5.0.

$C_{33}H_{28}O_8$ requires C = 71.7; H = 5.1 per cent.

[The monobenzoyl derivative requires C = 69.6; H = 5.4 per cent.]

Matairesinoldisulphonic Acid.—Matairesinol dissolved in cold concentrated sulphuric acid and yielded a fluorescent solution, which was diluted with water and neutralised with barium carbonate. From the filtered and concentrated solution, the barium salt separated on cooling in hard, well-formed prisms:

0.61 lost 0.0744 H_2O . H_2O = 12.2.

0.3558 gave 0.1130 $BaSO_4$. Ba = 18.8.

0.7338 gave 0.2334 BaSO₄. Ba = 18.8.

C₁₉H₁₅O₁₂S₂Ba, 5H₂O requires Ba = 18.8; H₂O = 12.3 per cent.

Matairesinolic Acid.

This compound was precipitated as a gummy mass when the solution of the resinol in excess of cold sodium hydroxide was acidified with acetic acid. Excess of acetic acid readily dissolved the amorphous substance, and in a short time the sparingly soluble, crystalline acid separated in beautiful hexagonal scales. Two preparations were analysed:

0.169 gave 0.3398 CO₂ and 0.1030 H₂O. C = 54.8; H = 6.8.

0.1526 „ 0.3038 CO₂ „ 0.0924 H₂O. C = 54.3; H = 6.7.

0.4101 lost, on drying at 20° and 20 mm, 0.0529 H₂O. H₂O = 12.9.

C₁₉H₂₂O₇, 3H₂O requires C = 54.8; H = 6.7; H₂O = 13.0 per cent.

The alcoholic solution of the acid was titrated:

0.1087 neutralised 2.58 c.c. N/10-NaOH. M.W. = 421.

C₁₉H₂₂O₇, 3H₂O requires 2.61 c.c. M.W. = 416.

Matairesinolic acid differs from its lactone in being easily soluble in alcohol, ammonia, and sodium carbonate. It is most easily recrystallised by dissolving in four times its weight of alcohol and diluting the solution with five times its own volume of water. It dissolves in about one hundred times its own weight of water at 70°, but at this temperature the solution soon turns turbid, owing to the formation of the more sparingly soluble lactone. Hydrochloric acid immediately precipitates the lactone from solutions of the acid. A preparation of the lactone obtained by boiling the acid with water and subsequent crystallisation from dilute acetic acid was found by melting point and analysis to be identical with the original matairesinol.

An acetone solution of the freshly prepared hydrated acid, containing 14.45 grams in 100 c.c. of solution, produced a rotation of -8.80°, corresponding with:

$[\alpha]_D^{20} - 3.04^\circ$ for the hydrated acid.

„ -3.46° „ „ anhydrous acid.

„ -3.65° „ „ lactone (calculated).

The observed value of $[\alpha]_D^{15}$ for the lactone is -4.89°; the lactone formation is thus accompanied by a change of optical activity, a phenomenon which has generally been observed in the case of the acids of the sugar group.

With the exception of the derivatives of the heavy metals, the salts of matairesinolic acid dissolve easily in water. The calcium salt is precipitated by alcohol, but the barium salt is not. Two preparations

of the amorphous *calcium* salt, obtained by precipitating the ammoniacal solution of the acid by means of alcoholic calcium chloride, gave $\text{Ca} = 10.4$ and 10.5 . $\text{C}_{19}\text{H}_{20}\text{O}_7\text{Ca}$ requires 10.0 per cent. The salt was distinctly alkaline to litmus paper.

Unlike pinoresinol, matairesinol yields no sparingly soluble potassium salt. The lactone dissolves easily in aqueous potassium hydroxide (one of alkali to two of water), but much solid alkali must be added before any salting-out occurs, and a very small quantity of water or alcohol redissolves the salt which is thus precipitated.

The authors have pleasure in recording that the expenses of this investigation have been largely defrayed by a grant from the Royal Society.

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LXXXIII.—2-Methyl-1:3-benzoxazine-4-one and Related Derivatives.

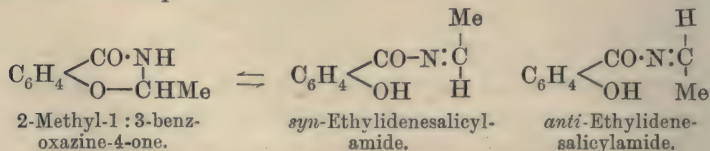
By WILLIAM LONGTON HICKS.

KEANE AND NICHOLLS (Trans., 1907, **91**, 266) showed that when benzaldehyde is condensed with salicylamide, 2-phenyl-1:3-benzoxazine-4-one is produced.

Titherley (*ibid.*, 1419) also prepared this compound and the two isomeric open-chain benzylidenesalicylamides.

Having regard to the importance of these compounds in connexion with the problem of the tautomerism and labile isomerism of the acylsalicylamides, it seemed essential to obtain the analogous methyl derivative, and also the two ethylidenesalicylamides.

The three compounds:

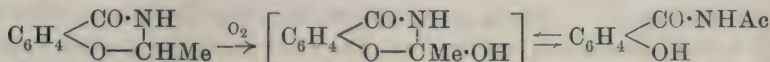


were obtained without any great experimental difficulty.

The *anti*-form is stable, and has no tendency to undergo any structural change. The *syn*-form, on the other hand, readily undergoes rearrangement on melting, and passes into 2-methyl-1:3-benz-

oxazine-4-one, from which it may again be formed by the action of alkalis. Here we have a complete analogy to the related phenyl compounds.

The relationship between 2-methyl-1:3-benzoxazine-4-one and *N*-acetylsalicylamide was proved by the oxidation of the former. The transformation may be explained by the following scheme:



Here, again, the behaviour is similar to that observed by Titherley in the case of 2-phenyl-1:3-benzoxazine-4-one.

EXPERIMENTAL

2-Methyl-1:3-benzoxazine-4-one.

Fifty grams of finely ground salicylamide were mixed with 50 grams of paraldehyde, and a stream of hydrogen chloride was passed in for one minute. The mixture was heated in a paraffin-bath to 50°, and after the ensuing violent reaction had subsided (about fifteen minutes), the temperature was raised to 75–80°, and there maintained for two hours. The product consisted of a hard cake, which, after cooling, was crushed and digested with 10 per cent. sodium hydroxide. The insoluble residue, now free from any unchanged salicylamide, was thoroughly washed with water, dried, and recrystallised from methyl alcohol. The yield of the pure substance was 65 grams:

0.2129 gave 0.5144 CO₂ and 0.1102 H₂O. C=65.91; H=5.75.

0.2836 „ 0.0301 NH₃. N=8.73.

C₉H₉O₂N requires C=66.13; H=5.53; N=8.59 per cent.

2-Methyl-1:3-benzoxazine-4-one crystallises from methyl alcohol in small needles, melting at 146°. It is fairly soluble in methyl or ethyl alcohols, acetone, or benzene, but much less so in ether, and it is insoluble in light petroleum. Its solutions give no coloration with ferric chloride. Cold sodium hydroxide does not dissolve it, and, on warming, hydrolysis occurs with the formation of acet-aldehyde and salicylamide.

Oxidation of 2-Methyl-1:3-benzoxazine-4-one.—Three grams of the substance were dissolved in 35 grams of ice-cold concentrated sulphuric acid, and a solution of 3.5 grams of chromium trioxide in 30 grams of glacial acetic acid was added at 0°. After half an hour, the temperature was allowed to rise to 10°, and the mixture was then poured into 1000 c.c. of ice-water. A white precipitate formed, which was collected, washed, dried, and crystallised from benzene, when it melted at 144°. It was completely soluble in

ammonium hydroxide, with a yellow colour, and was proved by analysis to be identical with *N*-acetylsalicylamide.

anti-Ethylidenesalicylamide.

Fifteen grams of salicylamide, 15 grams of sodium acetate, and 30 grams of paraldehyde were heated in a sealed tube at 150—180° for five hours. After cooling, the product was completely soluble in cold dilute sodium hydroxide. The alkaline solution, after being freed from excess of paraldehyde by extracting it with ether, was cooled in ice and treated with excess of dilute hydrochloric acid. An amorphous substance was precipitated, which was collected, washed, and dried on a porous plate in a desiccator. It was impossible to effect any purification, repeated precipitation from alkaline solution being unavailing. The substance melted very indefinitely at about 170°, and a nitrogen estimation (Kjeldahl) gave results only approximately correct. It gave a strong coloration with ferric chloride, and was hydrolysed to acetaldehyde and salicylamide on boiling with water. It showed no tendency to rearrange to the oxazone. This preparation was frequently repeated, but with results no more satisfactory, and as the compound had no great interest, further investigation was postponed.

syn-Ethylidenesalicylamide.

To a solution of 10 grams of 2-methyl-1:3-benzoxazine-4-one in 60 c.c. of pyridine were added 20 c.c. of aqueous sodium hydroxide (50 per cent.). The mixture was vigorously shaken for one and a-half hours, during which time the original red colour rapidly faded to a lemon-yellow. The solution was now diluted to 2 litres, and treated at 0° with excess of dilute hydrochloric acid. A white compound was precipitated, which was at first in an oily condition, but solidified after twelve hours. The yield was 8 grams:

0.3954 gave 0.0408 NH_3 . $\text{N} = 8.50$.

$\text{C}_9\text{H}_9\text{O}_2\text{N}$ requires $\text{N} = 8.60$ per cent.

syn-Ethylidenesalicylamide is not readily soluble in aqueous sodium hydroxide (10 per cent.), owing to the formation of a sodium salt; if a little alcohol is added before the alkali, immediate solution takes place. The addition of hydrochloric acid to the alkaline solution precipitates the compound in an oily form, which subsequently solidifies and then melts at 170—180°.

LXXXIV.—*The Absorption Spectra of Nicotine, Coniine, and Quinoline as Vapours, Liquids, and in Solution.*

By JOHN EDWARD PURVIS.

THE author has already presented the results of an investigation of the vapours of pyridine and some of its derivatives (this vol., p. 692). Since then, the vapours, the liquids, and solutions of nicotine, coniine, and quinoline have been investigated. The experimental methods employed in the study of the vapours are described in the earlier paper, and the methods for the study of the solutions have also been described before. The substances were redistilled several times before they were used.

Nicotine (α -pyridyl-*N*-methylpyrrolidine).—Hartley (*Phil. Trans.*, 1885, **176**, 471) examined the absorption of alcoholic solutions of this β -pyridine derivative, and found that with 0.367 gram in 36.7 c.c. of alcohol through a thickness of 1 mm. there was general absorption at about λ 2800; and through a thickness of 5 mm. the rays were absorbed at about λ 3132, but no band was observed. In the author's experiments with *N*/10-solutions, through 2 mm. thickness, the rays were absorbed at λ 2800; and, through 30 mm. thickness, at λ 3050; whilst for *N*/100-solutions, through 2 mm. thickness, the rays were absorbed at λ 2720, and, through 30 mm. thickness, at λ 2810, and no band was observed. But on examining *N*/1000-solutions, a band was discovered, and its absorption curve has been drawn (see Fig.). The general form of the curve is like that of pyridine (Hartley, *Trans.*, 1885, **47**, 685), but it is not so persistent. In this respect, its behaviour is similar to that of other pyridine derivatives. The weighting of the pyridine nucleus has also shifted the positions of the band and general absorption more towards the red end of the spectrum. The heads of the bands of pyridine and nicotine, expressed in oscillation frequencies, are:

Pyridine (Hartley)	3950
Nicotine	3820

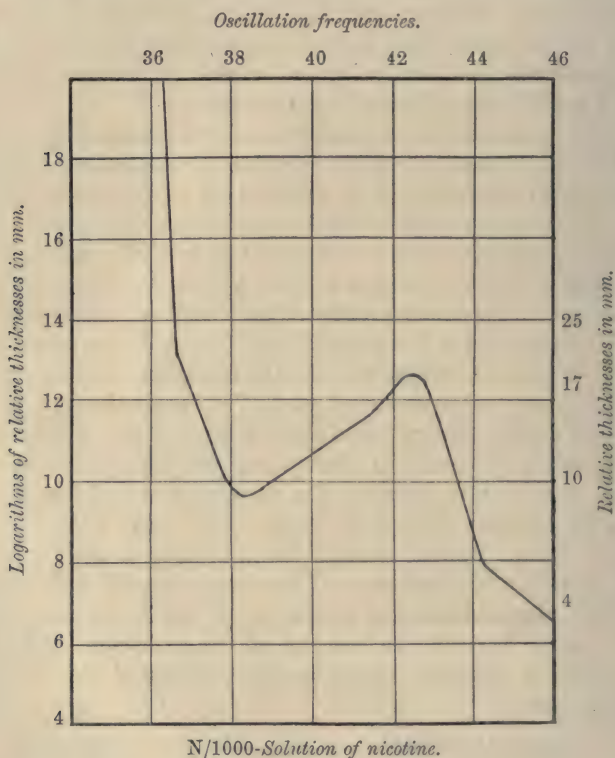
The vapour of nicotine was examined under the following conditions of temperature and pressure in a tube 200 mm. long:

t° .	Pressure in mm.	
15°	750	All the rays were transmitted to Cd 2144; the latter was well marked.
60	850	All the rays were transmitted to Cd 2194.
100	926	The rays were transmitted to about λ 2390; the rays were then absorbed to Cd 2329; the Cd lines 2321, 2313, 2306, 2288, 2267, 2265 being visible.

In another series of observations taken later, the following was observed :

t° .	Pressure in mm.	
14°	757	All the rays were transmitted to Cd 2144.
100	933	The rays were transmitted to about λ 2400 ; the rays were then absorbed to Cd 2329, and the series of Cd lines to λ 2265 was well marked.

In order to increase the amount of vapour, one drop of the mixture was introduced in the absorption tube. The temperature



of the bath was raised to 100°, and the absorption of the vapour observed at the following pressures :

t° .	Pressure in mm.	
100°	757	The rays were transmitted to Cd 2837 ; Cd 2748 was just visible.
100	627	The rays were transmitted to Cd 2837 ; Cd 2748 being visible.
100	27	„ „ „ „ λ 2820 ; Cd 2748 „ „

These observations indicate that (1) *N/1000-alcoholic solution*

of nicotine exhibits a band showing its relationship to pyridine; (2) the vapour of nicotine exhibits none of the series of narrow bands which have been observed by the author in pyridine vapour, but, as the temperature and pressure are increased, a strong absorption band is produced. The result is precisely similar to that observed in the vapours of the two dimethylpyridines and trimethylpyridine, and differentiates it from α -picoline vapour, which exhibited a few narrow bands, some of which are coincident with those of pyridine vapour (this vol., p. 692).

Coniine (α -N-propylpiperidine).—Hartley (Trans., 1885, **47**, 685) observed that alcoholic solutions of piperidine showed no bands in the ultra-violet, and that it was remarkably transparent. Coblenz (*Astrophys. J.*, 1904, **20**, 207) found a band in the ultra-red in the region of 3μ . The author has compared equimolecular solutions of piperidine and coniine, but no bands were observed in the ultra-violet, and the following numbers give the regions where general absorption begins:

Piperidine.

N/10-Solution ; through	2 mm. thick :	general absorption began at	λ 2185.
	30 " " "	" " "	λ 2345.
N/100-Solution ; through	2 " " "	" " "	λ 2180.
	30 " " "	" " "	λ 2220.

The results are in agreement with Hartley's observations.

Coniine.

N/10-Solution ; through	2 mm. thick :	general absorption began at	λ 2570.
	30 " " "	" " "	λ 3290.
N/100-Solution ; through	2 " " "	" " "	λ 2180.
	30 " " "	" " "	λ 2635.
N/1000-Solution ; through	2 " " "	" " "	λ 2130.
	30 " " "	" " "	λ 2265.

The vapour of coniine was also examined in a 200 mm. tube under the following conditions of temperature and pressure:

t° .	Pressure in mm.	
15°	740	All the rays were transmitted to Cd 2194.
30	784	" " " Cd 2194.
45	810	" " " Cd 2239.
60	840	" " " Cd 2265.
75	870	" " " Cd 2265 ; but they were weak between 2370 and Cd 2329.
90	900	The rays were transmitted to λ 2390, and after that they were absorbed ; only the Cd lines 2329, 2321, 2313, 2288, and 2265 being well marked.
100	916	The rays were transmitted to λ 2410 ; then they were absorbed, but the Cd 2329, 2321, 2313, 2288, and 2265 were again well marked.

In another series of observations, a drop of the liquid coniine was placed in the absorption tube so that it contained more vapour, and the following series of observations was made :

t°	Pressure in mm.	
100°	9	The rays were transmitted to Cd 2264, although they were scarcely visible between λ 2400 and the Cd line 2329.
100	309	" " " "
100	739	" " " "
17	9	The rays were transmitted to Cd 2194, which was well marked.
17	309	" " " "
17	739	" " " "

These results show that (1) alcoholic solutions of coniine exhibit no absorption bands, and that they are remarkably transparent. This result is exactly similar to that of piperidine solutions as first noted by Hartley; (2) the vapour of coniine shows none of the series of narrow bands like those observed by the author in the vapour of piperidine (*loc. cit.*); but, as before, by increased temperature and pressure, a weak absorption band is produced.

Quinoline.—Hartley (Trans., 1885, **47**, 685) has pointed out that an alcoholic solution of a synthetic preparation of this substance exhibited an absorption band between λ 317 and λ 310; and that a natural specimen gave three bands, the positions of which were λ 317— λ 310, λ 308— λ 303, λ 303— λ 289. The author has examined *N*/1000-solutions of freshly distilled quinoline, and finds three bands similar to these.

The vapour of quinoline was examined in a 200 mm. tube at the following temperatures and pressures :

t°	Pressure in mm.	
15.5°	765	Complete transmission of rays to Cd 2144.
30	809	Transmission of rays to Cd 2144, although they were weak between λ 2620 and λ 2550.
45	835	The rays were transmitted to λ 2630, and then absorbed to about λ 2430 (the Cd 2573 being visible). From λ 2430, the rays were transmitted to Cd 2144.
60	865	The rays were absorbed between λ 2660 and λ 2380, and then transmitted to Cd 2144; Cd 2573 was just visible.
75	895	The rays were absorbed between λ 2700 and λ 2340, and then transmitted to Cd 2144.
90	925	The rays were absorbed between λ 2710 and Cd 2329. The Cd lines to 2144 were well marked, although weaker than at 895 mm. pressure.
100	941	The rays were absorbed between λ 2740 and Cd 2329; the latter was very weak, and the Cd lines beyond λ 2144 were well marked.

The vapour was also examined at a constant temperature of 14°, and under the varying pressures of 33 mm., 183 mm., 333 mm., 483 mm., 633 mm., and 763 mm., but no bands were observed. There was a complete transmission of rays to Cd 2144.

These results show that (1) an alcoholic solution of quinoline

exhibits three bands, as first noticed by Hartley; (2) the vapour of quinoline shows none of the various bands found by Hartley in the case of benzene vapour (*Phil. Trans.*, 1907, *A*, **208**, 475), and by the author in the case of pyridine vapour (this vol., p. 692), but it has one large band. The condensation of the benzene and pyridine nuclei to produce quinoline has completely destroyed the vibrations which produce the narrow absorption bands observed in the vapours of the two substances, but on increasing the temperature and pressure, a large absorption band is produced.

The spectra of nicotine, coniine, and quinoline in the liquid condition were also examined, and they were compared with those of pyridine, α -picoline, and piperidine. For this purpose one drop of each liquid was pressed between two thin plates of quartz, and these were firmly held in front of the slit of the spectroscope, whilst the light of the Cd spark was passed through for five minutes. No absorption bands were observed; and the following numbers represent the regions where general absorption began under these conditions:

Pyridine	λ 2780
α -Picoline	2830
Nicotine	2870
Quinoline	3340
Piperidine	2250
Coniine.....	2260

The remarkable transparency of liquid piperidine and coniine is very striking, and is similar to that of the solutions.

General Results.

The general results of these observations are:

(1) *N*/1000-alcoholic solution of nicotine exhibits an absorption band in the ultra-violet region of the spectrum analogous to that found in a solution of pyridine; the vapour of nicotine exhibits none of the series of narrow bands found in the vapour of pyridine; and the liquid nicotine, like that of pyridine, shows no selective absorption.

(2) *N*/10-, *N*/100-, and *N*/1000-alcoholic solutions of coniine show no bands of selective absorption, a result similar to that of solutions of piperidine; the vapour of coniine exhibits none of the series of bands found in the vapour of piperidine; and the liquid has no selective absorption, but, like piperidine, it is remarkably transparent.

(3) *N*/1000-alcoholic solution of quinoline has three bands in the ultra-violet, as observed by Hartley; the vapour of quinoline has no narrow bands analogous to those found in the vapours of benzene and pyridine, but only one large band; and liquid quinoline shows no selective absorption.

In the author's earlier paper on the absorption spectra of the vapours of pyridine and some of its derivatives, the presence of the numerous bands in pyridine was discussed from a consideration of the impacts of the molecules when in the vaporous condition (*loc. cit.*). The implied symmetry of such a molecule as pyridine or piperidine suggests a regular and rhythmical vibration or pulsation of the ring. When the substance is in solution or in the liquid condition, these vibrations or pulsations are constrained.

In solution, the solvent acts both as a constraint on the pulsations and as a barrier to the number of encounters. The fundamental vibrations of the molecule are predominant, and the result is shown in the absorptive effect on the radiant energy by the appearance of a single large band. In the liquid condition, these restraining influences are still more pronounced, and no band of selective absorption is observed. When, however, the substance is in the vaporous condition, the molecules are free from the restraining influences and, in addition to the fundamental vibrations producing strong absorption, other vibrations or pulsations are set in motion. The result is more complex and rhythmical, and it is manifested in a series of narrow bands which can be arranged in groups having equal differences of wave-lengths.

Now, solutions of piperidine exhibit an absorption band in the ultra-red, whilst in pyridine solutions the band is in the ultra-violet regions of the spectrum. The vapour of pyridine has a considerable number of narrow bands completely different from those observed in piperidine vapour. The liquids pyridine and piperidine show none of these bands, and the latter is remarkably transparent.

In coniine, nicotine, trimethylpyridine, the two lutidines, and α -picoline, the symmetry of the molecules is destroyed by the various side-chains, and to the restraining influence of the heavy side-chains on the vibrations of the nucleus are added the irregularity of the encounters. The result is that the nucleus does not vibrate in the same rhythmical manner. In α -picoline vapour, only a few of the narrow bands found in pyridine are observed; and, in the vapours of the two lutidines, trimethylpyridine, nicotine, and coniine, the narrow bands are completely absent. As regards quinoline, although there is an implied symmetry in the constitution of its molecule not possessed by the other substances, the pulsations characteristic of each separate nucleus are not maintained in combination, and the narrow bands shown by the vapours of benzene and pyridine are obliterated. The vapour of quinoline has one powerful absorption band, which is exhibited at increased temperatures and pressures.

In solutions of these substances, the series of narrow bands are

completely absent, and even the fundamental vibrations are considerably affected, as shown by the decreased persistence of the absorption band when the side-chains are increased in number, type, and weight. Whilst in the liquids the restraining influences are even more predominant, and the radiant energy is absorbed by the vibrating molecules, for there is no selective absorption.

In such investigations as these it is difficult to differentiate the possible effect of the radiant energy of the source of light. It is probable that light waves have an important influence on the vibrations of the molecules, and more particularly when the latter are in the vaporous condition, when they have more freedom of movement. If this influence is taken into consideration, it is more correct to say that the absorption bands are the result of such various forces as the radiant energy, the type of nucleus, the side-chains of the nucleus, the encounters of the molecules, and the constraint to which they are subjected as vapours, liquids, or in solution.

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LXXXV.—*Changes in Volume in the Formation of Dilute Solutions.*

By HARRY MEDFORTH DAWSON.

As a result of numerous investigations of the volume changes which accompany the formation, mixing, and dilution of solutions, a large mass of data has been accumulated, and these have been variously interpreted either in terms of the better known theories of solution or on the basis of certain somewhat specialised mechanical theories. From a careful study of the literature, it appears that the volume changes chiefly studied are those connected with aqueous solutions, and that comparatively little is known in reference to the volume changes which occur in the formation of dilute non-aqueous solutions.

In this paper an account will be given of experiments which contribute in some measure to the filling of this gap, and also to throw further light on the processes which are operative in the

formation of dilute solutions. Although it is improbable that these processes are different in the case of a dilute solution as compared with that in which the admixed components are brought together in more nearly equal proportions, it was thought that, for the particular object in view, a more legitimate basis of comparison would be afforded if dilute solutions were employed. Under such conditions, the particular properties of the solvent, in so far as they influence the change in volume, may be expected to exhibit themselves in a simpler manner than would be the case if these solvents were admixed with considerable quantities of a foreign substance.

In connexion with the change in volume which usually accompanies the formation of a (dilute) solution, it has been frequently assumed that this is due to a change in the volume of the solute, and thus has arisen the conception of a molecular solution-volume. It is probable (compare Tammann, *Zeitsch. physikal. Chem.*, 1896, **21**, 529) that this assumption is no more justifiable than that which would refer the entire change in volume to the solvent, and its use can only be condoned on the grounds of convenience and simplicity, and more particularly because there is at present no general method of determining the relative parts played by solvent and solute in connexion with the volume change.*

In the case of aqueous solutions, numbers representing "molecular solution-volumes" have been deduced for a large variety of substances (compare Traube, *Ahrens' Sammlung*, Vol. IV), and certain general relationships have been shown to exist as a result of the comparison of these numbers with one another. For non-aqueous solutions the data are much less numerous, although isolated density measurements, from which "molecular solution-volumes" can be calculated, are contained in many published papers (compare Traube, *Zeitsch. anorg. Chem.*, 1895, **8**, 12). Systematic investigations dealing with the subject have been carried out by Carrara and Levi (*Gazzetta*, 1900, **30**, ii, 197), Walden (*Zeitsch. physikal. Chem.*, 1907, **60**, 87), and Lumsden (*Trans.*, 1907, **91**, 24). In the course of investigations on the influence by the solvent on the rotatory power of dissolved ethyl tartrate, T. S. Patterson (*Trans.*, 1901, **79**, 167, 477; 1902, **81**, 1097; 1904, **85**, 1153; 1905, **87**, 313; 1908, **93**, 355, 936, and 1836) has also measured the "solution-volume" of this substance in a considerable number of different solvents, and by extrapolation of curves showing the dependence

* For the special case of solutions of an optically active substance, a method of determining the actual volumes occupied by the solute and solvent has been indicated by Winther (*Zeitsch. physikal. Chem.*, 1907, **60**, 590).

of the "solution-volume" on the concentration has estimated the magnitude of this for infinitely dilute solutions.

Carrara and Levi, as well as Walden, worked with non-aqueous solutions of electrolytes, and the chief result which follows from their measurements consists in the demonstration that the ionisation of a binary electrolyte is accompanied by a diminution in volume, which is independent of the nature of the electrolyte and of the solvent in which it is dissolved. It is evident that this contraction which accompanies the ionisation of an electrolyte, and which, according to Drude and Nernst (*Zeitsch. physikal. Chem.*, 1894, **15**, 79), is due to the action of the electrostatic field resulting from the ions, introduces a factor which must tend to complicate the relationships otherwise involved in the process of the formation of solutions, and on this account it was considered advisable to carry out the experiments described in this paper with non-electrolytes.

For the first series of experiments, iodine was selected as a suitable non-electrolyte, and for the choice of this particular substance several reasons may be assigned. In the first place, its elementary nature and its simple molecular structure are distinctly favourable to its suitability as compared with a substance consisting of complex polyatomic molecules. Secondly, the molecular weight of iodine has been determined in a large number of solvents, and these measurements have established the fact that iodine is always present in solution in the form of diatomic molecules. Thirdly, the fact that iodine gives, with different solvents, solutions which exhibit remarkable differences in regard to their selective absorption of visible light rays is in itself of sufficient interest to warrant an inquiry into the existence of a possible connexion between the volume changes on the one hand, and the optical properties on the other.

The iodine was dissolved in some fifteen different solvents, and from density measurements of the pure solvents and the corresponding solutions the "molecular solution-volume" was calculated from the equation:

$$\phi = \frac{M + g}{d} - \frac{g}{d_0} \quad (1).$$

in which g is the weight of solvent in which the molecular weight M of iodine is dissolved, and d_0 and d are the densities of the solvent and solution at the same temperature.

Although the conception of "molecular solution-volume" is made use of in recording the volume changes which have been observed, it should be stated that the chief reason for the adoption of this particular method of expressing the results is to facilitate the discussion of certain relationships which are said to exist between

the "molecular solution-volume" and other properties, and not because the author attaches any special significance to the quantity calculated by means of the above equation.

The solutions examined were made by weighing out quantities of resublimed iodine and of the purified solvent so as to obtain solutions containing approximately 50, 100, or 200 mols. of solvent per mol. of iodine. In certain cases the most dilute solution only could be obtained by reason of the limited solubility of the iodine, but for several solvents measurements were made for the three differently concentrated solutions. As will be seen from the percentage numbers in the third column of table I, the solutions examined are in all cases such as may legitimately be regarded as dilute solutions.

It is obvious that this circumstance necessitated the attainment of great accuracy in the density measurements in order that the probable error attaching to the calculated value of the "molecular solution-volume" should be kept within sufficiently narrow limits. With a pycnometer of large capacity, it is theoretically possible to carry out density determinations of almost any required degree of precision, but as Tammann has shown (*Zeitsch. physikal. Chem.*, 1895, **16**, 91), there is considerable difficulty in bringing the contents of such pycnometers into thermal equilibrium with the surrounding bath of constant temperature. On this account, preliminary measurements were made with pycnometers of 20—25 c.c. capacity, provided with capillary end-tubes of small diameter and carefully ground-glass stoppers. The pycnometers were filled by gentle suction, the effect of differential vaporisation of solvent and solute during the process of filling being eliminated by drawing some 10—20 c.c. of the solution over into a second pycnometer placed between the suction apparatus and the pycnometer in actual use. After approximate adjustment of the pycnometer at 18°, it was placed in a water-bath of about 200 litres capacity, the temperature of which varied less than 0.01°, and after about three-quarters of an hour the final adjustment was made for the temperature of 18.00°. Weighings were made on a special balance in a room of nearly constant temperature, and the weights reduced to a vacuum. Corresponding measurements of the density of solvent and solution were made at very nearly the same time, and by this means any small differences due to changes in the barometric pressure were eliminated. Under these conditions it was found that the requisite accuracy in the density measurements could be obtained with pycnometers of 20—25 c.c. capacity. There can be little doubt that results of greater precision would be possible by the use of the displacement method of Kohlrausch and Hallwachs

(*Ann. Phys. Chem.*, 1894, [iii], **53**, 14), but in view of the fact that fairly volatile solvents were amongst those which it was proposed to investigate, it was decided to make use of the pyknometer method.

As affording some criterion of the maximum precision attainable in the measurement of the "molecular solution-volume" for the various solutions, it may be stated that the actual differences between the volumes of the solution and of the solvent, when referred to the volume of the pyknometer most frequently used in the measurement (21.4 c.c.), vary from about 0.05 c.c. to 0.45 c.c. The precision actually obtained in independent determinations of the "molecular solution-volume" in a given case can be gauged from the fact that the extreme values do not differ by more than about 1 c.c. in the case of the most dilute solutions, whilst the divergence of the separate values in the case of the more concentrated solutions is from two to three times smaller.

The experimental data obtained in the examination of the various solvents are collected in table I. Under d_0 the densities of the liquids used in the preparation of the solutions are recorded. In some cases, individual measurements were made at different times with different samples of solvent, and in consequence two or more slightly different values have been used for the same solvent. The exact composition of the solutions is shown in the third column, which gives the number of grams of iodine per 100 grams of solvent. The fourth column gives the approximate number of molecules of solvent per molecule of iodine, the fifth the density of the solution, and the sixth the value of the "molecular solution-volume" calculated by means of equation (1).

From an inspection of the separate values of ϕ for any particular solvent, it is at once evident that the "molecular solution-volume" of the dissolved iodine is independent of the concentration within the limits of variation of the dilute solutions examined. This justifies the combination of the individual values for each solvent, and the numbers in the seventh column have been obtained by taking the arithmetic mean of the separate values in column 6. It will be observed that the order in which the solvents are arranged is determined by the magnitude of the "molecular solution-volume" of the iodine. The value of ϕ diminishes from 67.2 for a nitrobenzene solution to 50.5 for a solution of iodine in ethyl ether.

For the purpose of reference to a standard value, these "solution-volumes" may be conveniently compared with the molecular volume of free iodine. According to Billet (*Jahresber.*, 1855, 46), the density of solid iodine is 4.9173 at 40.3° and 4.825 at 107.0°; assuming that the coefficient of expansion is constant, this gives 51.3 for the molecular volume of solid iodine at 18°. This is

TABLE I.

Solvent.	d_0 .	Grams of iodine per 100 grams of solvent.	Approximate molar ratio.	d .	ϕ c.c.	Mean $(\phi - \phi_i)$ c.c.
Nitrobenzene	1.20547	4.1375	50	1.23890	67.6	+8.7
"	1.20547	2.0495	100	1.22220	67.1	
"	1.20541	1.0240	200	1.21380	67.0	
Methyl acetate	0.936577	3.4325	100	0.960641	66.5	+7.7
"	0.935068	3.4440	100	0.959208	66.3	
"	0.935068	1.7305	200	0.947276	65.8	
Carbon tetrachloride ...	1.59597	0.8308	200	1.60376	65.3	+7.3
"	1.59600	0.8271	200	1.60371	65.9	
"	1.59610	0.7335	225	1.60295	65.8	
"	1.59605	0.7270	225	1.602755	66.9	
Phenylacetoneitrile	1.01812	2.1730	100	1.03435	65.4	+6.8
"	1.01812	1.0770	200	1.02617	65.3	
Ethyl acetate	0.901687	5.7667	50	0.941282	64.4	+6.0
"	0.901640	2.8648	100	0.921419	64.6	
Chlorobenzene	1.10786	4.5215	50	1.14340	64.5	+5.8
"	1.10786	2.2900	100	1.12599	64.4	
"	1.10786	1.1350	200	1.11690	63.9	
Heptane	0.732804	1.2670	200	0.740375	63.3	+5.4
"	0.732809	1.2753	200	0.740398	64.5	
Ethylene bromide	2.18379	2.6765	50	2.21034	62.7	+4.1
"	2.18379	1.3326	100	2.19712	62.6	
Toluene	0.867665	5.5735	50	0.905360	61.8	+3.3
"	0.867665	2.7835	100	0.886602	61.8	
Methyl alcohol	0.798274	7.887	100	0.848149	62.2	+2.8
"	0.798274	4.0265	200	0.824037	61.1	
"	0.798274	4.014	200	0.824010	60.7	
Carbon disulphide	1.26618	6.7233	50	1.32426	60.9	+2.6
"	1.26618	3.3055	100	1.29496	61.3	
"	1.26620	1.7028	200	1.28112	61.0	
Ethyl alcohol	0.791541	11.2908	50	0.862780	59.7	+1.3
"	0.791502	5.5053	100	0.826555	60.1	
"	0.791502	2.7433	200	0.809087	59.7	
Pyridine	0.971036	6.4233	50	1.018955	57.7	-1.0
"	0.971036	3.2430	100	0.995456	57.3	
Ethyl iodide	1.939355	1.6370	100	1.957615	55.1	-3.2
"	1.939355	0.8153	200	1.948425	55.5	
Ethyl ether	0.715945	6.8605	50	0.757613	50.8	-8.0
"	0.715945	3.4245	100	0.736893	50.2	

identical with the value corresponding with the density recorded by Gay Lussac—4.948 at 17°.

The density of liquid iodine, according to Billet (*loc. cit.*), is 4.004 at 107.0° and 3.796 at 170.0°. If we extrapolate on the assumption that the expansion of supercooled iodine is the same as that for the substance between 107° and 170°, the value of 58.5 is obtained as the molecular volume of liquid iodine at 18°.

The equation $V_t = V_{107} + 0.055 (t - 107^\circ)$, from which this value is obtained, leads to 67.65 as the molecular volume at the boiling point of iodine ($184.35^\circ/760$ mm.), whereas the value found directly by Drugman and Ramsay (Trans., 1900, **77**, 1218), is 68.45.

The question as to whether the measured "solution-volumes" should be compared with the volume of solid iodine or that of liquid iodine is of some importance. According to Billet's data, the coefficient of expansion of liquid iodine is nearly four times as large as that of the solid. From this fact it is at once evident that if we compare the volume changes on solution with reference to the volume of solid iodine on the one hand, and of liquid iodine on the other, differences will be obtained, the relative magnitude of which will depend very much on the temperature. Now, Lumsden (*loc. cit.*) has shown that the "solution-volume" of a substance is either equal to the volume occupied by the pure liquid substance at the same temperature, or deviates from it by an amount which is the same for all temperatures. On the basis of this observation, it appears that the "solution-volumes" should be compared with the volume of the liquid rather than that of the solid solute. If the generalisation of Lumsden holds good for all solvents, the volume differences which are thus obtained should be independent of the temperature at which the actual measurements are made.

The numbers recorded under $(\phi - \phi_l)$ in the previous table are the differences between the "molecular solution-volume" of iodine in the different solvents and the volume of liquid iodine at the same temperature. These differences serve as a measure of the volume changes which take place in the formation of the solutions. The positive values correspond with an increase in volume, the negative values with a contraction.

By comparing the highest and lowest values obtained for the "molecular solution-volume" of iodine, we find a difference which amounts to 16.7 c.c., and this, when referred to the molecular volume of liquid iodine, represents a variation of 28.5 per cent. This difference, corresponding with the observed limits of variation of the volume changes which occur when relatively small quantities of iodine are dissolved in different solvents, is surprisingly large.

The further discussion of the observed volume changes may be conveniently deferred until after the communication of experimental data obtained in a second series of experiments in which the volume changes accompanying the formation of dilute solutions of naphthalene were measured. As in the case of the iodine solutions, the relative proportions of naphthalene and solvent were adjusted so as to give solutions containing approximately 50, 100, or 200 mols. of solvent per mol. of solute. The quantities of naphthalene

per 100 grams of solvent vary from about 0.7 to 4.0 grams; in all cases, therefore, the solutions may be considered as dilute. By reason of the smaller density of naphthalene as compared with that of iodine, the measured volume changes are in general appreciably larger; the actual values, reckoned on the basis of the capacity of the pycnometer, vary from about 0.19 c.c. to 0.9 c.c. Corresponding with this greater average value of the volume change, it is found that the separate values obtained for the "molecular solution-volume" of naphthalene in a given solvent are in much better agreement than the corresponding numbers for iodine.

The experimental data for the solutions of naphthalene are collected in table II. The arrangement of the numbers is precisely the same as that adopted for the iodine solutions, the solvents being arranged according to the magnitude of the "molecular solution-volume" of the solute.

TABLE II.

Solvent.	d_0 .	Grams of naphth- alene per 100 grams of solvent.	Approx- imate molar ratio.	d .	ϕ .	Mean ϕ .	$(\phi - \phi_i)$.
Ethylene bromide.....	2.18376	1.3565	50	2.15094	125.50	125.5	+2.0
„ „	2.18376	0.6769	100	2.16715	125.50		
Nitrobenzene	1.20538	2.0793	50	1.20106	125.0	124.85	+1.35
„	1.20538	1.0428	100	1.20322	124.7		
Carbon disulphide.....	1.26617	3.3472	50	1.256635	124.85	124.85	+1.35
„ „	1.26617	1.6765	100	1.261285	124.89		
Chlorobenzene	1.108644	2.1780	50	1.106861	124.23	124.3	+0.8
„	1.108644	1.0890	100	1.107727	124.33		
Pyridine	0.971116	3.2130	50	0.972955	123.85	123.8	+0.3
„	0.971116	1.6201	100	0.972075	123.70		
Toluene	0.867712	2.7802	50	0.871577	123.35	123.3	-0.2
„	0.867712	1.3918	100	0.869678	123.25		
Ethyl iodide	1.939355	1.6274	50	1.912855	123.16	123.15	-0.35
Carbon tetrachloride...	1.59605	1.6627	50	1.58235	122.71	122.75	-0.75
„ „	1.59605	0.8309	100	1.58910	122.82		
Heptane	0.733829	2.5460	50	0.739257	122.87	122.75	-0.75
„	0.733829	1.2794	100	0.736595	122.62		
Methyl acetate	0.935068	1.7472	100	0.936766	122.50	122.5	-1.0
Ethyl acetate.....	0.902993	2.8884	50	0.906699	121.18	121.15	-2.35
„ „	0.902993	1.4470	100	0.904874	121.16		
Methyl alcohol	0.795106	4.0253	100	0.802991	120.20	120.0	-3.5
„ „	0.795106	2.0090	200	0.799135	119.84		
Ethyl alcohol... ..	0.792496	2.7862	100	0.798158	119.30	119.15	-4.35
„ „	0.792496	1.3888	200	0.795371	119.00		
Ethyl ether	0.716020	3.4565	50	0.724957	112.86	112.9	-10.6
„ „	0.716020	1.7204	100	0.720512	112.90		

According to Lossen and Zander (*Annalen*, 1884, **225**, 111), the density of liquid naphthalene at its melting point (79°) is 0.982, and its change of volume with temperature is given by the equation:

$$V_t = V_{79}\{1 + 0.0382314(t - 79) + 0.0041550(t - 79)^2 + 0.0039971(t - 79)^3\}.$$

From these data we obtain by extrapolation $\phi_l = 123.5$ as the molecular volume of liquid naphthalene at 18° . The values of $(\phi - \phi_l)$ in the last column of the table are calculated on this basis.

As in the case of iodine, the formation of dilute solutions of naphthalene from the liquid solute is sometimes accompanied by an increase in volume, and in other cases by a decrease. The largest and smallest observed "molecular solution-volumes" differ to the extent of 12.6 c.c., and this, when referred to the volume of liquid naphthalene at 18° , corresponds with a variation of 10.2 per cent. The corresponding differences in the case of iodine are 16.7 c.c. and 28.5 per cent., and from this it is evident that the observed percentage variation of the "molecular solution-volume" is much greater for iodine than for naphthalene.

In proceeding to the further discussion of the two series of experimental data, it may at once be pointed out that the order of the solvents is not the same in the two series when the solvents are arranged according to the magnitude of the "molecular solution-volume" of the dissolved substance. The existence of certain isolated relationships between the two series is, however, not to be denied, and the most noteworthy instance is to be found in the fact that the "molecular solution-volume" of both iodine and naphthalene is very much smaller when dissolved in ethyl ether than it is in any of the other solvents examined. Further, it is seen that both substances have a large "molecular solution-volume" when dissolved in nitrobenzene; this solvent stands at the head of one series, and is the second member of the other. Apart from such isolated instances of parallel behaviour, it is, however, quite certain that the two sequences are essentially different. A measure of this difference is afforded by the numbers in table III, which shows the extent to which the volume changes are dependent on the nature of the dissolved substance. The second column gives the difference between the "solution-volumes" of naphthalene and iodine; the third the ratio of these numbers.

From this table it is seen that the difference between the "molecular solution-volumes" varies from 56.3 in the case of methyl acetate solutions to 67.8 in that of solutions in ethyl iodide. The variation of volume ratio is from 1.85 in methyl acetate to 2.24 in ethyl ether. Although for certain closely related solvents, such as methyl and ethyl acetate and methyl and ethyl alcohol, the volume differences and ratios are approximately equal, the general

TABLE III.

Solvent.	$\Phi_{\text{naphthalene}} - \Phi_{\text{iodine}}$	$\Phi_{\text{naphthalene}}/\Phi_{\text{iodine}}$
Nitrobenzene	57.65 c.c.	1.86
Methyl acetate	56.3	1.85
Carbon tetrachloride.....	56.95	1.86
Ethyl acetate.....	56.65	1.88
Chlorobenzene	60.0	1.93
Heptane	58.85	1.92
Ethylene bromide.....	62.9	2.00
Toluene	61.5	1.99
Methyl alcohol	58.7	1.96
Carbon disulphide.....	63.75	2.04
Ethyl alcohol.....	59.35	1.99
Pyridine	66.3	2.15
Ethyl iodide ..	67.85	2.23
Ethyl ether ..	62.4	2.24

conclusion to be drawn from the wide limits of variation exhibited by the numbers in the above table is that the observed changes in volume cannot be explained completely by reference to any particular property or properties of the pure solvents without taking into account the nature of the dissolved substance. The difference in sequence can only be accounted for by supposing that the expansion or contraction effects are in some measure due to the action of forces, the magnitude of which, in the case of a particular solvent, depends on the specific nature of the dissolved substance. Such a view is tantamount to the assumption that chemical forces are involved, and that the operation of these leads to the formation of compounds by union of the dissolved substance with the solvent.

In the case of iodine solutions, evidence of various kinds has been put forward in support of this view, and the different colours exhibited by iodine when dissolved in different liquids are supposed to be due to variations in the extent to which such combination takes place. For solutions of naphthalene there are no corresponding observations which might be used to test the validity of the hypothesis of chemical combination, or even to differentiate between the behaviour of the various solvents.

In these circumstances it seems permissible to inquire to what extent the relative changes in volume in the different solvents can be accounted for in the case of either of the dissolved substances by reference to the properties of the solvents.

According to the kinetic theory, a liquid substance may be regarded as an aggregate of rapidly moving molecules subjected to forces of attraction which give rise to the so-called internal pressure. From the purely physical point of view, the different solvents used in this investigation may be regarded as media differentiated from one another by their internal pressure values. If, now, a liquid solute is dissolved in a relatively large quantity of

some solvent, and the resulting change in volume of the system is debited to the solute, it might be supposed that the magnitude of the volume change would be more or less simply related to the difference between the internal pressures of the liquid solute and of the resulting solution. If the solution is sufficiently dilute, its internal pressure will be approximately the same as that of the pure solvent, and the volume change might be expected to depend on the difference between the internal pressures of the liquid solute and of the solvent. According as the internal pressure of the solvent is greater or less than that of the solute, the formation of the solution would be attended by contraction or expansion.

If, on the other hand, the solvent alone is supposed to undergo a change in volume, we may suppose that this is due to the alteration of the internal pressure which is produced when the dissolved substance is added to the solvent. Contraction or expansion will then be expected according as the internal pressure is increased or diminished by the added solute.

The part played by the internal pressure in connexion with the properties of solutions and more especially of aqueous solutions has been investigated in detail by Tammann (*Ueber die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen*, 1907), who has shown that the volume changes which occur when aqueous solutions are mixed together or diluted can be satisfactorily accounted for in terms of the internal pressure if the volume change is debited to the solvent. In particular, the volume changes which occur on the neutralisation of aqueous solutions of acids and bases can be interpreted in a simple manner, and the variation of these changes in volume with the temperature has been recently found by Freund (*Zeitsch. physikal. Chem.*, 1909, **66**, 555) to be in harmony with the requirements of Tammann's theory.

In spite of this, the contrary assumption, according to which the solute alone suffers a change of volume, appears to have been more frequently made. In a somewhat special form this view has been adopted by Patterson (*Trans.*, 1901, **79**, 167), who infers that the "molecular solution-volume" of a substance should diminish as the internal pressure of the solvent increases. Up to the present, the data necessary for subjecting this hypothesis to a critical examination have not been available. This has not been solely due to the lack of suitable data relating to volume changes in different solvents, but equally to the fact that the internal pressure values were unknown except in a few isolated cases. As a result of Walden's investigations on the connexion between the physical properties of liquid substances, the aspect of our knowledge of internal pressures has been completely changed. By reference to

a large mass of experimental data, it has been shown (*Zeitsch. physikal. Chem.*, 1909, **66**, 385) that the internal pressure of a liquid at its boiling point is intimately connected with its surface tension and critical pressure, and various formulæ have been obtained from which the internal pressure can be calculated. In the case of non-associated liquids, the different methods of computation lead to results which are in satisfactory agreement. For associated liquids the agreement is not nearly so good, and in all cases the internal pressures computed from surface tension data appear to be abnormally small.

The significance of the internal pressure in connexion with the properties of liquids has also been emphasised by Traube (*Zeitsch. physikal. Chem.*, 1909, **68**, 289) and by Winther (*ibid.*, 1907, **60**, 590, 641, 685), and these authors have deduced internal pressure values for a considerable number of liquids at 0°.

The data recorded by Walden, Traube, and Winther will now be utilised to examine whether there is any connexion between the "molecular solution-volume" of either of the solutes used in this investigation and the internal pressure of the solvent. In table IV the solvents are arranged according to their internal pressures. The second column gives Walden's data for the various solvents at their respective boiling points; the third gives Traube's and the fourth Winther's data for 0°, the pressures being recorded in atmospheres. The "molecular solution-volumes" of naphthalene and iodine are shown in the fifth and sixth columns, and the seventh gives Patterson's values for the extrapolated "molecular solution-volume" of ethyl tartrate at 20° in infinitely dilute solution:

TABLE IV.

Solvent.	Internal pressure (Walden).	Internal pressure (Traube).	Internal pressure (Winther).	$\phi_{\text{naphthalene}}$	ϕ_{iodine}	$\phi_{\text{ethyl tartrate}}$
n-Heptane.....	955	—	—	122·75	63·9	—
Ethyl ether	1220	990	1220	112·9	50·5	—
Toluene.....	1356	1180	1638	123·3	61·8	174·8
Ethyl acetate	1390	1140	1486	121·15	64·5	—
Methyl „	—	1280	1709	122·5	66·2	—
Carbon tetrachloride.	1450	1305	1824	122·75	65·8	173·9
Chlorobenzene	1500	1340	—	124·3	64·3	—
Nitrobenzene	1610	—	—	124·85	67·2	174·0
Ethyl iodide.....	1730	—	—	123·15	55·3	178·3
Ethylene bromide ...	1790	1570	2114	125·5	62·6	176·8
Pyridine	1840	—	—	123·8	57·5	—
Carbon disulphide ...	2155	1980	2220	124·85	61·1	—
Ethyl alcohol	(2850)	2160	2030	119·15	59·8	164·0
Methyl „	(3430)	3440	2420	120·0	61·3	159·3

In reference to the first two series of internal pressure values, it is to be noted that, in spite of the temperature differences involved,

both lead to the same sequence of solvents if we except the case of toluene and ethyl acetate, the internal pressures of which are, however, very nearly equal. From a comparison of Traube's numbers with those of Winther it is evident that although the latter are in general considerably greater than the former, they also give rise to the same sequence if we except the relative positions occupied by carbon disulphide and ethyl alcohol. The parallelism of the three series is all the more striking when it is remembered that the methods of evaluation employed by the three authors are essentially different in kind. If now the corresponding series of "molecular solution-volumes" are examined, there appears to be no simple connexion between these and the internal pressures of the solvents, and this is true whether the dissolved substance is naphthalene, iodine, or ethyl tartrate.

The assumption, made by Patterson in connexion with the explanation of the variation of the rotatory power of an optically active substance in different solvents, that the "molecular solution-volume" may be used as a means of determining approximately the internal pressure of the solvent in which it is dissolved, appears therefore quite unjustifiable. Although earlier observations of the rotatory power of ethyl tartrate in different solvents appeared to show a connexion between the rotatory power and the "molecular solution-volume," Patterson has more recently shown that this is not generally the case (compare *Trans.*, 1908, **93**, 355).

The proof of the absence of any connexion between internal pressure and "molecular solution-volume" has, of course, no direct connexion with Patterson's theory relating to the influence of internal pressure on rotatory power, and, indeed, strong evidence in favour of the existence of a connexion between these two magnitudes has been brought forward by Winther (*loc. cit.*).

The observed lack of any connexion between the internal pressure of a solvent and the "solution-volume" of a dissolved substance appears to be at variance with Walden's conclusion (*Zeitsch. physikal. Chem.*, 1907, **59**, 385) that the "molecular solution-volume" is connected with the co-volume of the solvent—the smaller the co-volume the greater the "solution-volume" of the solute. The simple relationship between internal pressure and co-volume, which is indicated by the form which van der Waals' equation assumes when applied to a liquid, namely,

$$\text{Internal pressure} \times \text{co-volume} = \text{constant},$$

suffices to show that the experimental results obtained in this investigation are opposed to the existence of any such relationship as that claimed by Walden. Since the solvents used by Walden are ionising solvents consisting in most cases of associated molecular

aggregates, and since the dissolved substance, tetraethylammonium iodide, is partly ionised in the various solutions, it is at once apparent that Walden's experimental conditions are by no means of the simplest kind. Moreover, the fact that the co-volumes are calculated from Traube's empirical formula, and represent the relatively small differences between the measured molecular volumes and the estimated sum of the volumes of the atoms and linkings in the molecule of the solvent, is sufficient in itself to raise doubts in regard to the validity of the conclusion which Walden has drawn.

A brief reference may now be made to the extreme opposite view, which attributes the volume change occurring in the formation of a solution to a change in the volume of the solvent. From the equation:

$$\frac{M+g}{d} - \left(\frac{M}{d_0} + \phi_l \right) = \phi - \phi_l \quad (2)$$

it is clear that $(\phi - \phi_l)$ is the actual change of volume which occurs in the formation of the solution. If this change in volume is due to the alteration of the internal pressure which results when the solute is added to the solvent, the internal pressure must increase or diminish according to whether contraction or expansion occurs in the formation of the solution. If ΔP is the alteration of the internal pressure for a dilute solution containing one gram-molecule of solute in V litres, ΔV the change in volume, and β the compressibility of the solvent, then, since

$$\beta = \frac{\Delta V/V}{\Delta P} \text{ and } \Delta V = \phi - \phi_l,$$

we obtain

$$\Delta P = \frac{1}{V\beta}(\phi - \phi_l) \quad (3).$$

From this equation and the data for the solvents common to tables I and II, it follows that the addition of iodine in small quantity lowers the internal pressure in the case of eleven solvents, and raises it in the case of three. On the other hand, the data for naphthalene indicate a diminution of internal pressure for five solvents and an increase in the case of nine. For eight of the fourteen solvents in question—pyridine, toluene, carbon tetrachloride, heptane, methyl acetate, ethyl acetate, methyl alcohol, and ethyl alcohol—the volume changes are of opposite sign according to whether iodine or naphthalene is dissolved. For each of these solvents it would follow that the internal pressure is increased by one of the dissolved substances and diminished by the other.

In the case of the remaining six solvents which exhibit volume changes of the same sign, we may compare the magnitudes of the internal pressure changes produced by equimolar quantities of

iodine and naphthalene. If these changes are denoted respectively by ΔP_i and ΔP_n , and the volume changes by $(\phi - \phi_l)_i$ and $(\phi - \phi_l)_n$ then from equation (3) we obtain:

$$\frac{(\phi - \phi_l)_i}{(\phi - \phi_l)_n} = \frac{\Delta P_i}{\Delta P_n} \quad (4).$$

Substituting the observed volume changes in this equation, we obtain the following values for the relative changes of internal pressure produced by iodine and naphthalene: ethyl iodide 9.0, chlorobenzene 7.2, nitrobenzene 6.4, ethylene bromide 2.0, carbon disulphide 2.0, ethyl ether 0.75. The large variation met with in this series is not less striking than the inequality of the sign of the internal pressure change found in the case of the other eight solvents. Both facts seem to show that an explanation of the observations cannot be obtained on the assumption that the volume changes are due to a change in the volume of the solvent under the influence of a variation of the internal pressure. At the same time it may be noticed that ethyl ether, which gives the largest contraction for both dissolved substances, is the most compressible solvent investigated, and that nitrobenzene, which gives the largest expansion in the case of iodine and the largest but one in the case of naphthalene, is probably the least compressible of the various solvents. A comparison of the coefficients of compressibility with the volume changes indicates, however, that in general there is no simple connexion between the two quantities.

From the above theoretical considerations it appears that the observed volume changes cannot be interpreted on the basis of the supposed changes in internal pressure. It also seems unlikely that any satisfactory explanation can be obtained on the basis of any mechanical (or electrical) theory which involves the simple consideration of the radii of the spheres of influence of the molecules of solvent and solute as in that put forward by Holmes (Trans., 1906, **89**, 1774; compare also Holmes and Sageman, Trans., 1907, **91**, 1606; 1909, **95**, 1919).

As already indicated on p. 1049, the fact that the volume changes, in passing from one solvent to another, are very largely dependent on the specific nature of the dissolved substance seems to afford strong evidence in favour of the formation of molecular aggregates containing solvent and solute molecules. An examination of the experimental facts found in the case of iodine solutions from this point of view will form the subject of a further communication.

The chief results obtained in this paper may be summarised as follows:

1. The changes in volume which occur in the formation of dilute

solutions of iodine and naphthalene have been measured for fourteen different solvents.

2. The observed changes in volume vary to the extent of 16.7 c.c. per gram-molecule of iodine, and 12.6 c.c. per gram-molecule of naphthalene.

3. The order of the solvents, when arranged according to the magnitude of the change in volume, is quite different for the two dissolved substances.

4. The observed volume changes cannot be accounted for by reference to the internal pressures or other properties of the solvents; in particular it is shown that there is no general connexion between the "molecular solution-volume" of a substance and the internal pressure of the solvent.

5. Walden's view, that the "molecular solution-volume" of a substance diminishes as the co-volume of the solvent increases, is shown to be erroneous.

6. The dependence of the volume changes on the specific nature of solvent and solute points to the formation of molecular aggregates (solvates).

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LXXXVI.—*The Triazo-group. Part XIII. Triazomethylcarbimide (Triazomethyl isocyanate).*

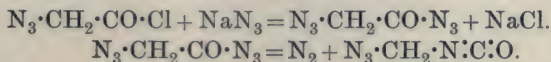
By MARTIN ONSLOW FORSTER and ROBERT MÜLLER.

THE present investigation was undertaken with the object of adding one more type to the series of simply constructed, aliphatic triazocompounds which have been examined during the past three years. Triazomethylamine, it was thought, in view of its low molecular weight, its high percentage of nitrogen, and the theoretical possibility of converting it into the still more curious pentazomethane, $\text{N}_3\cdot\text{CH}_2\cdot\text{N}_2$, would prove to be a fertile subject for research.

The prospect of obtaining triazomethylamine by the action of alkaline hypobromite on triazoacetamide was not a favourable one, Hofmann having found that the application of his well-known reaction to chloroacetamide led to symmetrical chloromethylchloroacetylcarbamide (*Ber.*, 1885, **18**, 2375); the isolation of chloromethylamine, in fact, was not to be expected, because interaction between hydrogen and chlorine would be almost certain to follow association of the halogen with a carbon atom bearing the amino-group. The knowledge that derivatives of triazoacetic acid retain

the substituent more tenaciously than those of chloroacetic acid led us to attempt the Hofmann reaction with triazoacetamide, but nothing of a basic character besides ammonia was produced; the presence of alkali azide in the residual liquid, however, encouraged us to continue the investigation, as it pointed to behaviour on the part of the triazo-group quite distinct from that which characterises it in the original material.

Another mode of attacking the problem was accordingly sought, and, recalling the facility with which cinnamenylcarbimide may be obtained from cinnamoylazoimide (Forster, *Trans.*, 1909, **95**, 433), we prepared triazomethylcarbimide from triazoacetyl chloride and sodium azide, in the hope that by some process which would leave the azoimide complex undisturbed, the remaining nitrogen atom in triazomethylcarbimide, or in a carbamide derivative obtained from it by the action of bases, might be transformed into the amino-group:



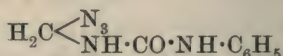
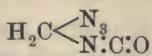
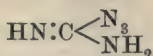
It should be explained that when the description of cinnamenylcarbimide appeared in March, 1909, it was believed to be the earliest record of this process for obtaining isocyanates. An account of the formation of these compounds by removing nitrogen from acyl azoimides, published by G. Schroeter (*Chem. Zeit.*, 1908, **32**, 933), however, escaped our notice until June, 1909, when the detailed account of Schroeter's investigation appeared (*Ber.*, 1909, **42**, 2336). This publication led R. Stoermer (*Ber.*, 1909, **42**, 3133) to announce that the same reaction had been observed by him nearly nine years previously, but had remained unpublished excepting in dissertations.

The first step in the direction indicated demanded an improvement in the preparation of triazoacetyl chloride, which before had been obtained in small quantities only; this has been accomplished by heating triazoacetic acid with thionyl chloride, and distilling the triazoacetyl chloride from about 15 per cent. of triazoacetic anhydride produced along with it. Interaction between triazoacetyl chloride and sodium azide led at first to some very alarming explosions, but conditions of moderate safety have now been ascertained, and although the hazardous nature of our experiences led us finally to discontinue the investigation, enough has been learned concerning triazomethylcarbimide to warrant a description of the substance being presented.

Triazoacetyl azide, the compound intermediate between triazoacetyl chloride and triazomethylcarbimide, has not been isolated, and we believe it to be a very dangerous substance. The com-

paratively low temperature at which it suffers explosive decomposition precludes the possibility of preparing it from sodium azide and undiluted triazoacetyl chloride, and although the use of ether as diluent has led to the only satisfactory results which have been obtained, the course of the reaction is not altogether trustworthy. It sometimes happens that the double decomposition between the azide and the chloride is not complete before the conversion of the triazoacetyl azide into triazomethylcarbimide has begun, and as a more elevated temperature is required for the latter transformation, the former is liable to proceed beyond control, and an explosion follows. Moreover, the sensitive character of triazomethylcarbimide itself renders it necessary to carry through the twofold change within the shortest possible limits of time, and the difficulty of retarding the first change while accelerating the second one is considerable.

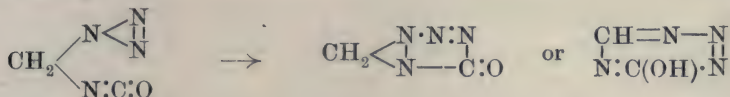
An examination of triazomethylcarbimide furnished an immediate explanation of the failure to prepare triazomethylamine by the Hofmann reaction, treatment with cold water being sufficient to remove the azoimide complex in the form of hydrazoic acid. The same change occurs when triazomethylcarbamide and phenyltriazomethylcarbamide are treated with warm water or cold alkali carbonates, and it is therefore not surprising that the action of alkali hydroxide on triazoacetobromamide should result in the production of alkali azide. It seems remarkable that the replacement of carboxyl in triazoacetic acid by the isocyanate or substituted amino-group should modify so profoundly the behaviour of the azoimide radicle. The description of triazomethane given by Dimroth and Wislicenus (*Ber.*, 1905, **38**, 1573) does not state whether the triazo-group is readily detached from carbon in that substance, but it was shown that in the case of 1:2-bistriazoethane this effect is produced only by continued action of hot alcoholic alkali (*Trans.*, 1908, **93**, 1070). Moreover, disruption between carbon and nitrogen in triazoacetic acid takes place only as a consequence of destroying the azoimide nucleus and the formation of an imino-compound (*loc. cit.*, 72). It is evident, therefore, that the union between a carbon atom and the triazo-group is rendered much less intimate by associating the carbon with another atom of nitrogen. In this connexion it is worth while to recall the fact that carbaminoiminoazoimide (Thiele, *Annalen*, 1892, **270**, I) loses the triazo-group very readily to alkali, and in this compound, also, there is another atom of nitrogen associated by a single linking with the carbon which carries the triazo-group:



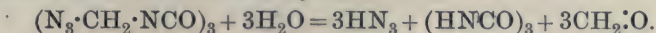
Carbaminoiminoazoimide. Triazomethylcarbimide. Phenyltriazomethylcarbamide.

It may be stated, in fact, that the behaviour of triazomethylcarbimide reveals the triazo-group in a condition of association with carbon which is even more easily dissolved than that prevailing in the acyl azides, since these are obtainable in aqueous systems.

One of our objects in preparing triazomethylcarbimide was to ascertain whether any atomic rearrangement would take place between the triazo-group and the unsaturated carbimide nucleus, for example:

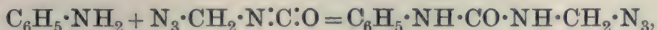


Such a transformation might have been expected from the readiness with which the azoimide complex unfolds itself to take part in additive actions, but the inquiry in this direction has been hampered by the facility with which the carbimide undergoes conversion into the *isocyanurate*, a change common to *isocyanates* generally. The product being a white, odourless solid, we were prepared to find that the change represented above had actually taken place, but there seems little doubt that it consists of tristriazomethyl *isocyanurate* on account of its behaviour towards weak alkali hydroxide, which resolves it into hydrazoic acid, cyanuric acid, and formaldehyde:

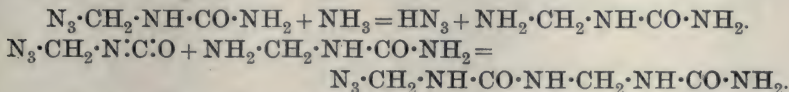


In this respect there is complete analogy between our polymeride and the substance obtained by Hofmann from trimethyl *isocyanurate* and phosphorus pentachloride (*Ber.*, 1886, **19**, 2088); the latter compound, trichloromethyl *isocyanurate*, should arise also by polymerisation of the chloromethylcarbimide recently described by Schroeter (*Ber.*, 1909, **42**, 3358).

Although the presence of the *isocyanate* group is associated in triazomethylcarbimide with transformations characteristic of that class, for instance, conversion into phenyltriazo-methylcarbamide by aniline:

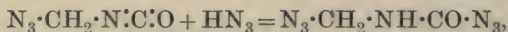


the unusually sensitive condition of the azoimide nucleus leads to complications when the substance is treated with ammonia or water. In the former reaction, there is produced, in addition to triazomethylcarbamide, a derivative of this which probably arises in the following manner:

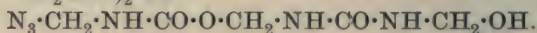
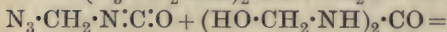
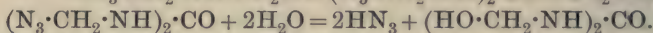
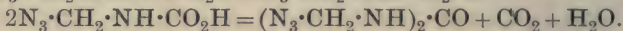
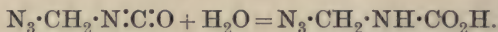


When water acts on the carbimide, a liquid substance is produced

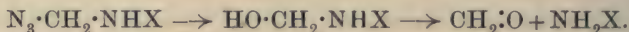
together with an insoluble solid, hydrazoic acid being set free; as the liquid is very explosive and contains more nitrogen than the original material, we regard it as triazomethylcarbamyl azide, but it could not be purified. Since phenylcarbamyl chloride and bromide arise by the action of halogen hydrides on phenylcarbimide, it seems reasonable that triazomethylcarbamyl azide should be formed, in view of the large proportion of hydrazoic acid set free:



and the insoluble solid would be the product of the following changes:



There remains one point of general interest to be noted. When the derivatives of triazomethylcarbimide are heated with aqueous alkali hydroxide, the odour of formaldehyde quickly becomes perceptible, ammonia and hydrazoic acid being simultaneously produced. This is readily understood by recognising that exchange of the triazo-group for hydroxyl in such substances would lead to derivatives of hydroxymethylamine, the hypothetical formaldehyde-ammonia:



The liberation of formaldehyde is thus explained in conformity with the behaviour of α -amino-alcohols.

EXPERIMENTAL.

Attempt to Prepare Triazomethylamine, $\text{N}_3 \cdot \text{CH}_2 \cdot \text{NH}_2$.

Our first experiment in the above direction consisted in applying to triazoacetamide that modification of Hofmann's original process which has been described by François (*Compt. rend.*, 1908, **147**, 680). Five grams of triazoacetamide were dissolved in 20 c.c. of water in which calcium carbonate was suspended, slowly treated with 9 grams of bromine, and mixed with ice-cold 30 per cent. potassium hydroxide as soon as effervescence had subsided. After two hours the temperature was raised to about 100° by passing the liquid through a narrow tube bent several times up and down in the manner described by François, the tube being immersed in boiling water. On subjecting the product to distillation in a current of steam, aqueous ammonia was condensed, and the residue in the flask contained potassium azide. This experiment, although

a failure, revealed the distinctive property acquired by the triazo-group when the atom of carbon to which it is attached becomes directly associated with another atom of nitrogen, because it has been shown that potassium azide is not produced when potassium triazoacetate is heated with excess of alkali. It indicated, further, the necessity of proceeding to triazomethylamine by an indirect method.

Preparation of Triazoacetyl Chloride.

The method by which triazoacetyl chloride was obtained on a former occasion (Trans., 1909, **95**, 200) being unsuited to the production of large quantities, the following course was adopted. Triazoacetic acid from 100 grams of ethyl triazoacetate was heated at 60—70° during two hours under 2—3 mm. pressure in order to remove water, and transferred to a reflux apparatus connected with a tube containing calcium chloride; 87 grams of thionyl chloride were added, and the temperature slowly raised, when brisk evolution of sulphur dioxide and hydrogen chloride took place. Heating was continued, latterly on the water-bath, until the gases had been removed, when the residue was distilled under diminished pressure. The chloride boiled at 43—44°/14 mm., and had sp. gr. 1·3640/13°; with due observance of precautions in hydrolysing the ester and in the removal of alcohol from the solution of potassium triazoacetate, the yield of chloride is about 75 per cent. of that calculated from the weight of ester employed, the residue in the flask consisting of very impure triazoacetic anhydride from which a certain amount of triazoacetic acid may be recovered. Before applying the chloride to the preparation of triazomethylcarbimide, it is advisable to ensure the absence of thionyl chloride or products containing sulphur. A convenient way of doing this consists in treating a portion with a solution of stannous chloride in hydrochloric acid, and warming until nitrogen ceases to be liberated; on diluting with a considerable proportion of water, the liquid should remain colourless, presence of sulphur being indicated by darkening due to stannous sulphide.

Triazomethylcarbimide (Triazomethyl isoCyanate), $N_3 \cdot CH_2 \cdot N:C:O$.

The preliminary steps towards preparing this compound led to somewhat alarming occurrences. On adding 0·5 gram of sodium azide to 0·7 gram of triazoacetyl chloride, action began without delay, accompanied by vigorous effervescence, and culminating after fifteen seconds in a terrific explosion. The test was then repeated with rather smaller quantities, the containing vessel being surrounded with ice, but the detonation, although delayed perhaps

a few seconds, was just as imposing, and was accompanied by a flash of yellow light. It was therefore necessary to use a diluent.

Expecting that the boiling point of triazomethylcarbimide would approach 120° under atmospheric pressure, we aimed at selecting a solvent from which it might be distilled without carrying the medium, and accordingly added 3.5 grams of sodium azide to 5 grams of triazoacetyl chloride in twice its volume of *o*-nitrotoluene, but here again the outcome was astonishing, for an explosion occurred after a very short interval; these results must be attributed to a rise in the temperature of the liquid above the detonating point of triazoacetyl azide, because triazoacetyl chloride is a comparatively harmless material. The next attempt was made with a mixture of ether and benzene, but this experiment failed because the production and decomposition of the triazoacetyl azide was not complete within the period devoted to the trial, namely, three to four hours, so that although triazomethylcarbimide was certainly produced, it was mixed with a large proportion of triazoacetyl chloride. Substituting bromobenzene for benzene led to no more fortunate result, but we ultimately found that under certain conditions the *isocyanate* may be prepared by using ether alone.

Seven grams of sodium azide were added to a mixture of 10 grams of triazoacetyl chloride with 40 c.c. of ether (dried over sodium) in a flask connected with a reflux condenser and a tube of calcium chloride; action soon became evident from the ebullition of the solvent, and was allowed to proceed for about an hour. The flask was then warmed cautiously on a water-bath during three hours to complete the double decomposition between the chloride and the azide, after which the ether was gradually boiled away, and the residue heated alone for the last two hours of the seven occupied by the experiment. It was then evident from the odour of the product that transformation into *isocyanate* had been complete, because although the smell of this material is horribly pungent, that of triazoacetyl chloride is very penetrating, and has a distinctive quality which makes it perceptible in those cases when it is still present.

The combined product from two such experiments was then freed from ether under atmospheric pressure, and distilled with the aid of the pump, when the *isocyanate* passed over as a clear, colourless liquid at $44\text{--}45^{\circ}/32$ mm., $39^{\circ}/26$ mm., and $35.5^{\circ}/19$ mm.:

0.1483 gave 72.7 c.c. N_2 at 20° and 764 mm. $N=56.38$.

0.0818 „ 40.4 c.c. N_2 „ 20° „ 772 mm. $N=57.42$.

$C_2H_2ON_4$ requires $N=57.14$ per cent.

Although it would appear from this description that the preparation of triazomethylcarbimide is a simple one, a successful

result has been obtained in very few of the thirty or forty experiments which have been made. Moreover, the course of the reaction is so treacherous that after an alarming explosion which took place recently during the removal of the solvent, and which must have been due to imperfect decomposition of the triazoacetyl azide, although the action had apparently proceeded in the manner described, we have reluctantly abandoned the investigation of this interesting substance.

The vapour of triazomethylcarbimide exerts an overpowering effect on the mucous membrane of the eyes and nose, and the liquid produces painful sores if allowed to come in contact with the skin. The freshly distilled isocyanate has sp. gr. 1.2580/18°, and when covered with aqueous sodium carbonate quickly dissolves, yielding sodium azide. The action of concentrated sulphuric acid is violent, but not explosive, while effervescence with stannous chloride in hydrochloric acid is very brisk.

Action of Water.—Several grams of freshly distilled triazomethylcarbimide were covered with a few c.c. of cold water, and left in an open beaker during three to four weeks. Action took place immediately, hydrazoic acid passing into the water, and being easily recognised after a short interval by the powerful odour, while that of the isocyanate was destroyed in the course of a few hours. At the conclusion of the experiment a white solid remained suspended in the water, and a heavy, colourless oil, which did not appear to be undergoing any further change, was also observed. The solid was removed mechanically, being rather sticky, washed with ether, and extracted with hot acetone, which dissolved a small quantity of the polymeride, melting at 153°. The snow-white residue was insoluble in boiling chloroform or benzene, and in hot pyridine; it intumesced at 242°, forming a clear, yellow liquid a few degrees above this temperature. When heated with 20 per cent. aqueous potassium hydroxide, the substance did not dissolve, and but a moderate proportion of hydrazoic acid was eliminated; ammonia was set free, and the odour of formaldehyde became perceptible. It effervesced mildly with concentrated sulphuric acid:

0.1706 gave 57.6 c.c. N₂ at 22° and 764 mm. N=38.45.

C₅H₁₀O₄N₆ requires N=38.53 per cent.

The heavy oil from which the foregoing product had been separated was extracted with ether, and treated with animal charcoal and anhydrous sodium sulphate; on evaporating the filtrate in a vacuum, a viscous, odourless oil remained, and did not become solid during four months in the desiccator. The liquid was insoluble in dilute hydrochloric acid or sodium carbonate, but gradually changed under the influence of the latter into a white

solid, whilst hydrazoic acid was eliminated. The first attempt to estimate nitrogen resulted in a violent explosion:

0.1153 gave 65.5 c.c. N_2 at 18° and 768 mm. $N = 66.32$.

$C_2H_3ON_7$ requires $N = 69.50$ per cent.

The oil underwent violent decomposition with concentrated sulphuric acid, which developed the odour of hydrogen cyanide; when heated with 30 per cent. potassium hydroxide it gave formaldehyde, ammonia, and a large proportion of potassium azide.

Tristriazomethyl isocyanurate, $(N_3 \cdot CH_2 \cdot NCO)_3$.

On one occasion the distillation of the *isocyanate* was accompanied by a curious phenomenon. As the first few drops fell into the receiver, a particle of white solid was noticed in suspension, and as the operation proceeded this grew so rapidly that by the time the liquid had passed over, its transformation into the solid was almost complete. Some of this material afterwards appeared in the tube of the condenser, but we are still ignorant as to the cause of the change, which was not observed in any succeeding preparation; there was reason to think, however, that in this particular experiment the accompanying ether had been removed more thoroughly than usual.

The snow-white compound is odourless, and gives sluggish effervescence with concentrated sulphuric acid; it is insoluble in boiling alcohol, and only very sparingly soluble in hot chloroform and acetone. The substance dissolves somewhat readily in cold pyridine, however, separating in colourless needles on dilution with water, and melts, evolving gas, at 153° :

0.0670 gave 33.2 c.c. N_2 at 22° and 770 mm. $N = 56.89$.

$C_2H_2ON_4$ requires $N = 57.14$ per cent.

A 20 per cent. aqueous solution of potassium hydroxide dissolves the compound when gently warmed, developing the odour of formaldehyde; by the use of more dilute alkali the production of cyanuric acid was established, and acidification of the resulting liquid with dilute sulphuric acid gave hydrazoic acid. Thus the behaviour indicates a polymeride of the *isocyanate* rather than a simple transformation product in which the triazo-group has undergone rearrangement into a tetrazole derivative.

Phenyltriazomethylcarbamide, $C_6H_5 \cdot NH \cdot CO \cdot NH \cdot CH_2 \cdot N_3$.

The calculated amount of freshly distilled aniline was mixed with three or four parts of ether (dried over sodium), cooled in ice, and slowly added to the *isocyanate* dissolved in the same proportion of ether. After a short interval, flat, lustrous, colourless needles

separated, and as the substance was found to undergo decomposition very rapidly in the dissolved state, especially if the solution is warmed, recrystallisation was effected by dissolving it in cold acetone, diluting with water, and filtering the felted mass of snow-white needles without delay:

0.1100 gave 35.7 c.c. N_2 at 23° and 766 mm. $N=36.88$.

$C_8H_9ON_5$ requires $N=36.65$ per cent.

Phenyltriazomethylcarbamide melts at 120° ; it is freely soluble in organic liquids excepting petroleum, which does not dissolve it on boiling. It is rapidly attacked by hot water, which eliminates the triazo-group in the form of hydrazoic acid. Brisk effervescence occurs with concentrated sulphuric acid, and gas is liberated also by stannous chloride in hydrochloric acid.

Action of Sodium Carbonate.—A freshly prepared specimen of the carbamide was covered with a dilute aqueous solution of the alkali, which at once converted it into a stiff paste; this quickly became hard again, and was then recrystallised from a small quantity of hot alcohol. Stellate aggregates of snow-white needles were deposited, melting at 147° with vigorous intumescence:

0.0391 gave 6.0 c.c. N_2 at 22° and 768 mm. $N=17.58$.

$C_8H_{10}O_2N_2$ requires $N=16.88$ per cent.

Absence of the triazo-group was indicated by the action of concentrated sulphuric acid, which merely dissolved the substance without evolving gas, and on examining the sodium carbonate from which the carbamide had been filtered, this was found to be rich in sodium azide.

Triazomethylcarbamide, $N_3 \cdot CH_2 \cdot NH \cdot CO \cdot NH_2$.

Triazomethylcarbimide in ether (dried over sodium) was cooled with ice, and treated with a solution of ammonia in the same solvent until the odour of isocyanate was destroyed. White flocks appeared almost immediately, followed more slowly by clumps of long, lustrous, colourless needles. The solvent was decanted, the solid quickly drained on earthenware, and stirred with cold benzene to remove any unchanged isocyanate. After recrystallisation from a concentrated solution in dry acetone, which was allowed to evaporate in the desiccator, the substance melted at 56° :

0.0686 gave 35.9 c.c. N_2 at 22° and 776.5 mm. $N=60.55$.

$C_2H_5ON_5$ requires $N=60.87$ per cent.

Triazomethylcarbamide is freely soluble in cold acetone and insoluble in chloroform or benzene; cold water dissolves it readily, and the odour of hydrazoic acid becomes quickly noticeable on warming the solution. The substance froths vigorously with con-

centrated sulphuric acid, developing the odour of hydrogen cyanide; gas is liberated also by stannous chloride in hydrochloric acid. Hot aqueous 30 per cent. potassium hydroxide gives rise to ammonia, formaldehyde, and potassium azide.

A second product of the action of ammonia on triazomethylcarbimide was revealed on allowing the ether decanted from the foregoing compound to evaporate in a vacuum desiccator. The pasty residue had the odour of hydrazoic acid, and left a snow-white, crystalline mass when drained on earthenware, melting with decomposition at 227°

0.0999 gave 45.4 c.c. N_2 at 24° and 776.5 mm. $N=52.07$.

$C_4H_9O_2N_7$ requires $N=52.41$ per cent.

This compound was insoluble in cold acetone and water, but dissolved in the latter on warming, when hydrazoic acid was liberated. It effervesced with concentrated sulphuric acid, producing the odour of prussic acid; hot 30 per cent. potassium hydroxide resolved it into formaldehyde, ammonia, and hydrazoic acid. As already explained, we regard this substance as arising from the action of triazomethylcarbimide on the hypothetical aminomethylcarbamide resulting from replacement of the azoimide complex in triazomethylcarbamide by the amino-group.

We have pleasure in expressing our thanks to Mr. S. H. Newman for preparing a considerable quantity of triazoacetic acid and triazoacetyl chloride required as material for this investigation.

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LXXXVII.—*Some Derivatives of Tetramethyl Ferrocyanide.*

By ERNALD GEORGE JUSTINIAN HARTLEY, B.A. (Oxon.).

IN a recent paper on the osmotic pressure and electrical conductivity of calcium ferrocyanide solutions (Berkeley, Hartley, and Stephenson, *Phil. Trans.*, 1909, A, **209**, 319), it was shown by the authors that the usual formula given for this substance— $Ca_2FeC_6N_6$ —is not in accordance with the experimental results obtained on the assumption that Boyle's law holds good for dilute solutions, taking into consideration the fact that it is a highly ionised salt.

A double molecular weight corresponding with $Ca_4Fe_2C_{12}N_{12}$ was provisionally suggested, and it was found that the numbers obtained

from measurements of the same physical properties of potassium ferrocyanide were not incompatible with the assumption of a similar double molecule. On the other hand, it was pointed out that there is some evidence from Buchbock's work on the freezing points of solutions of tetraethyl ferrocyanide (*Zeitsch. physikal. Chem.*, 1897, **23**, 157) that the simple formula is the correct one.

Tetraethyl ferrocyanide is prepared from silver ferrocyanide and ethyl iodide, and it is possible that the radicle FeC_6N_6 may have a different constitution in a derivative of this salt from that which it has in potassium or calcium ferrocyanides, just as the nitriles and isonitriles are produced from potassium and silver cyanides respectively.

It seemed therefore desirable to prepare if possible some derivative of potassium or calcium ferrocyanide not ionised in solution, and to determine whether its molecular weight agreed with the simple or the double formula.

In the original paper on the preparation of tetraethyl ferrocyanide (*Ber.*, 1888, **21**, 935), Freund showed that this substance is not formed by the usual process of passing hydrogen chloride into a mixture of the acid and alcohol, the result being in this case an imido-ether, which is very unstable, and consequently unsuitable for a molecular weight determination. With the view of obtaining the lower homologue, tetramethyl ferrocyanide, another fairly general way of preparing methyl esters was therefore tried, namely, the action of methyl sulphate on a salt of the acid. This method can be applied in two ways. In one, methyl sulphate is simply distilled with the dry salt when the ester passes over; for example, the chloride, formate, and benzoate have been so prepared. A second means of effecting the reaction is to treat an aqueous solution of the salt with methyl sulphate.

Werner and Seybold recently (*Ber.*, 1904, **37**, 3658) thus prepared several esters, which cannot be formed directly from the acid and alcohol. After trying the second method unsuccessfully, it was found that dry potassium ferrocyanide is capable of reacting with methyl sulphate at a moderate temperature, and although tetramethyl ferrocyanide itself is not one of the products of the reaction, several compounds closely related to this are formed, an account of the preparation and properties of which seems to be of sufficient interest to be communicated to the Society.

The operation was carried out in the following manner. Fifteen grams of very finely powdered anhydrous potassium ferrocyanide were added to an excess (70 c.c.) of methyl sulphate in a flask connected with an air condenser and a calcium chloride tube to exclude moisture. The flask and its contents were heated in a

water-bath at about 80—90° for from four to six hours with frequent shaking. The solid matter had then changed to a more bulky, whitish substance (A),* usually tinged with blue. The contents of the flask were brought on to a hot filter, a hardened paper being used and suction applied until as much liquid as possible had been extracted, when the solid matter was washed with 25 c.c. of methyl sulphate, the filtrate being received in another vessel and used for further preparations.

The liquid portion, on cooling, deposited a small crop of white crystals, often slightly coloured blue (B). The liquid from the crystals was poured into a distilling flask fitted to a second similar flask in the usual way for distilling under diminished pressure. When a very low pressure had been obtained, the contents of the flask were heated in a boiling-water bath. In this way the excess of methyl sulphate distilled off fairly rapidly, leaving a brown liquid which, on cooling, solidified to a crystalline mass (C).

The three products of the reaction, A, B, and C, were examined, with the following results.

The substance A was soluble in water. It gave a precipitate of Prussian blue with ferric chloride and a white precipitate with barium chloride, and the characteristic potassium platinichloride with platinic chloride. It was almost completely soluble in hot methyl alcohol, the insoluble portion which alone gave the first two above reactions being evidently some unchanged potassium ferrocyanide and some potassium sulphate. The methyl-alcoholic solution deposited white crystals on cooling, having the appearance of potassium methyl sulphate.

An estimation of the potassium as platinic chloride (Found, $K=25.98$. Calc., $K=26.03$ per cent.) and also the quantitative conversion of the salt into potassium sulphate (Found, $K=25.84$; and 26.06 . Calc., $K=26.03$ per cent.) confirmed this.

The substance B deposited from the liquid was freed from methyl sulphate as far as possible by spreading on a porous plate, and was then dried in an exhausted desiccator over sulphuric acid.

It is very soluble in water, moderately so in methyl alcohol, and practically insoluble in ethyl alcohol and all the ordinary organic solvents. The solution in water has an acid reaction, and gives a white precipitate with barium salts, evidently of barium sulphate. It gives none of the usual reactions for iron salts, nor for ferro- or ferri-cyanides. On boiling with potash it is decomposed, giving an odour of isocyanides, and a brown precipitate is formed, which

* As a suitable nomenclature for some of the substances formed has not yet been definitely decided on, they will be referred to through this paper, for convenience, as A, B, C, etc.

dissolves in hydrochloric acid and gives a precipitate of Prussian blue with potassium ferrocyanide. Platinic chloride gives a precipitate, which, examined under the microscope, is seen to consist of non-isotropic crystals of a fern-like appearance, when formed from a concentrated solution. The substance itself was readily crystallised from hot methyl alcohol. The crystals so obtained are quite stable in the air, and lose no weight at 100° . They begin to show signs of softening at about 220° and then gradually decompose, but no sharply defined melting point could be obtained. On ignition, a residue of practically pure ferric oxide is left, and a complete analysis of the salt, in which the iron was determined by igniting the substance, dissolving the ferric oxide in concentrated hydrochloric acid, and reprecipitating with ammonia in the usual way, showed that no iron is lost by volatilisation.

The whole of the SO_4 is precipitated by barium chloride. The analytical results, carried out with material recrystallised twice, are as follows:

0.4984 gave 0.0822 Fe_2O_3 . $\text{Fe}=11.54$.

0.3449 „ 0.3222 BaSO_4 . $\text{SO}_4=38.44$.

0.2216 „ 30.03 c.c. N_2 at N.T.P. $\text{N}=16.99$.

0.2543 „ 0.2734 CO_2 and 0.0941 H_2O . $\text{C}=29.34$; $\text{H}=4.14$.

Total found = 100.45.

Another preparation recrystallised three times from methyl alcohol gave $\text{SO}_4=38.35$; $\text{Fe}=11.46$ per cent. The consideration of the formula to be deduced from these numbers will be dealt with later on in the paper.

The substance C, which was evidently the main product of the reaction, was freed from liquid as far as possible by spreading it on a porous plate and keeping in a vacuum over sulphuric acid. It is readily soluble in water, methyl and ethyl alcohols, but not in other ordinary solvents. It gives a similar platinichloride to the substance B, but differs from this in its extreme solubility in ethyl alcohol and also in that it gives no precipitate with barium chloride.

On keeping it for several days in a vacuum, it became partly converted into a form which is insoluble in ethyl alcohol and gives a precipitate of barium sulphate with barium chloride.

An attempt was made to recrystallise it from ethyl alcohol, but the solution was unstable, and a considerable quantity of the insoluble form was soon deposited. An analysis of the insoluble variety purified by washing several times with ethyl alcohol gave the following result:

0.4151 gave 0.3827 BaSO_4 . $\text{SO}_4=37.94$.

0.5163 „ 0.0868 Fe_2O_3 . $\text{Fe}=11.76$.

As these numbers agree pretty closely with those found in the analysis of B, a complete analysis was made of the substance purified by recrystallisation from methyl alcohol. The results were as follows:

0.5000 gave 0.0822 Fe_2O_3 . $\text{Fe}=11.51$.

0.5120 „ 0.4763 BaSO_4 . $\text{SO}_4=38.27$.

0.2023 „ 27.04 c.c. N_2 at N.T.P. $\text{N}=16.76$.

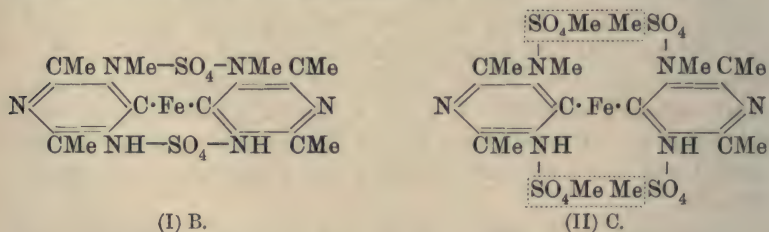
0.2382 „ 0.2565 CO_2 and 0.0871 H_2O . $\text{C}=29.39$; $\text{H}=4.09$.

$\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_6\text{S}_2\text{Fe}$ requires $\text{Fe}=11.28$; $\text{SO}_4=38.68$; $\text{N}=16.95$;
 $\text{C}=29.02$; $\text{H}=4.07$ per cent.

The composition of the substance (which may be written $\text{FeC}_{12}\text{H}_{20}\text{N}_6(\text{SO}_4)_2$ or $\text{FeC}_6\text{N}_6\text{Me}_6\text{H}_2(\text{SO}_4)_2$) is thus identical with that of the compound B. The properties of the compound C, and its gradual conversion into a sulphate having the above composition, can be best explained by assuming the reaction to take place in the following way.

First, tetramethyl ferrocyanide and potassium methyl sulphate are formed by the interaction of potassium ferrocyanide and methyl sulphate, and the former, behaving as a basic substance, can combine either with an acid or with methyl sulphate, just as ammonia and amines generally can combine with both the above.

The analytical numbers obtained for B point to its being a compound of one molecule of tetramethyl ferrocyanide with one molecule of methyl sulphate and one of sulphuric acid, which may be represented provisionally by (I) writing for convenience the ferrocyanogen molecule as being composed of two tricyanogen rings:



There is at present no evidence as to which of the six nitrogen atoms is in combination with these two groups.

The substance C, which is soluble in ethyl alcohol, can then be represented by (II).

On keeping for a long time in a vacuum, it gives off the two molecules of methyl sulphate enclosed by the dotted lines, and then becomes converted into B. This is confirmed by the fact that on heating the compound C by means of an oil-bath to about 150° , methyl sulphate (Found, $\text{C}=18.65$; $\text{H}=4.96$. Calc., $\text{C}=19.04$;

H=4.79 per cent.) distils over, and the insoluble variety B is at once produced.

A determination of the SO_4 in a portion of B prepared in this way, and recrystallised three times from methyl alcohol gave the following numbers:

0.4122 gave 0.3856 BaSO_4 . $\text{SO}_4 = 38.49$.

The same conversion into a sulphate is effected by adding concentrated sulphuric acid drop by drop to a solution of C in ethyl alcohol, when crystals of B are immediately deposited. A determination of SO_4 in these crystals, washed with ethyl alcohol, and dried in a vacuum, but not recrystallised, gave these numbers:

0.3910 gave 0.3602 BaSO_4 . $\text{SO}_4 = 37.90$.

$\text{C}_{12}\text{H}_{20}\text{O}_8\text{N}_6\text{S}_2\text{Fe}$ requires $\text{SO}_4 = 38.68$ per cent.

A further confirmation of the above formula for C is given by a determination of the iron made on a portion of the substance, purified as far as possible by spreading on a porous plate, and keeping for a few hours in a vacuum over sulphuric acid:

1.0172 gave 0.1126 Fe_2O_3 . $\text{Fe} = 7.75$.

$\text{C}_{16}\text{H}_{32}\text{O}_{16}\text{N}_6\text{S}_4\text{Fe}$ requires $\text{Fe} = 7.48$ per cent.

Lastly, the two formulæ proposed explain why a precipitate with barium chloride is produced with B but not with C, the former being the sulphate, the latter the methosulphate of a base.

Preparation and Analysis of the Platinichloride.

Two specimens of the above were prepared from the substances B and C respectively by precipitating a fairly strong aqueous solution with a slight excess of hydrogen platinichloride. The crystalline precipitate was washed and dried at 100° . It can be obtained in small but well-formed crystals by dissolving in a large quantity of boiling water and allowing the solution to cool slowly.

In the first two analyses the iron was separated from the platinum by precipitating the latter as sulphide in an acid solution of the residue obtained by ignition of the salt. As the platinum was found to carry down traces of iron, in the third analysis the separation was more thoroughly effected by redissolving the impure platinum and reprecipitating as ammonium platinichloride. The analytical results were as follows:

(a) Platinichloride prepared from C:

0.5813 gave 0.1626 Pt. $\text{Pt} = 27.97$.

0.5813 „ 0.0660 Fe. $\text{Fe} = 7.94$.

(b) Platinichloride prepared from B :

0.4969 gave 0.1393 Pt. Pt = 28.03.

0.4969 „ 0.0577 Fe₂O₃. Fe = 8.14.

0.3440 „ 0.2598 CO₂ and 0.0841 H₂O. C = 20.61 ; H = 2.73.*

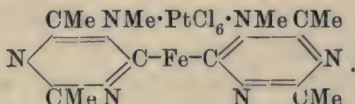
(c) A mixture of above recrystallised from water :

0.5260 gave 0.1457 Pt. Pt = 27.70.

0.3320 „ 0.2443 CO₂ and 0.0764 H₂O. C = 20.08 ; H = 2.57.

C₁₂H₁₈N₆Cl₆FePt requires Pt = 27.45 ; Fe = 7.89 ; C = 20.30 ;
H = 2.55 per cent.

The substance may be graphically represented as follows :



Comparing this with the formula given to B, it will be seen that the H₂SO₄ group is split off, and PtCl₆ has replaced the other SO₄ radicle.

It must clearly be understood that this structure is not considered adequate to represent completely the reactions involved in the formation and properties of these compounds, since it would be necessary to show the three pairs of nitrogen atoms unsymmetrically placed with regard to each other. It is hoped, however, that further experiments with these and the ferricyanides† will throw considerably more light on the structure of the ferrocyanogen radicle.

It has not at present been found possible to give a quite definite explanation of one step in the reaction that has been described, namely, the formation of two MeHSO₄ groups in the substance C.

It seems likely that it is due to moisture introduced at some time during the experiment, in all probability mainly in the filtration.

Water reacts very readily with methyl sulphate to form methyl hydrogen sulphate, and it is extremely difficult to ensure the complete absence of its vapour during the whole course of operations. Some experiments have been carried out, using very carefully dried materials, and filtering without exposing the liquid to the outside air by means of a porcelain filtering tube fitted in

* In this analysis, lead chromate was used, and for decomposing the oxides of nitrogen, a silver spiral, which appears not to have been quite efficient as the water was slightly acid. This accounts for the carbon and hydrogen being rather too high. In the subsequent analysis, lead chromate and a reduced copper spiral were employed, which proved quite satisfactory.

† A preliminary experiment has shown that potassium ferricyanide reacts in a similar way with methyl sulphate.

the neck of the flask in which the reaction took place, but so far definite results have not been obtained, the products being in part the same as before. It is hoped, however, that further experiments will clear up this point.

A suitable nomenclature for these substances is desirable; at present it is proposed to describe B as hexamethyl ferrocyanogen dihydrogen sulphate, and the platinum derivative as hexamethyl ferrocyanogen platinichloride.

An attempt was made to prepare the free base from hexamethyl ferrocyanogen dihydrogen sulphate by precipitating the whole of the SO_4 radicle with baryta. The experiment was carried out both with aqueous and methyl-alcoholic solutions, the baryta being added gradually from a burette until nearly the whole of the SO_4 was precipitated.

The liquid was then filtered and evaporated in a vacuum over sulphuric acid. In both cases the only product was a brown, semi-liquid mass, which could not be obtained in a crystalline form, and decomposed rapidly in aqueous solution, giving a precipitate apparently of ferric hydroxide. It was alkaline to litmus, and had an unbearable odour. It was not found possible to obtain it in a sufficiently pure condition for analysis.

I am glad to take the opportunity to express my sincerest thanks to Lord Berkeley for placing at my disposal his laboratory and all the chemicals and apparatus for this research, and for much assistance and advice during its progress. Also to his assistant, Mr. Frederick Carter, for his most valuable help in carrying out a great part of the preparations and analyses recorded in this paper; also to Mr. H. B. Hartley and Mr. D. H. Nagel, of Balliol and Trinity Colleges, Oxford, for their kindness in giving me permission to use their laboratory and apparatus for all the combustions required.

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LXXXVIII.—*Sodium Succinates.*

By HUGH MARSHALL and DAVID BAIN (Carnegie Research Scholar).

In a paper by Marshall and Cameron (Trans., 1907, **91**, 1519) there were communicated the results of an investigation of the various potassium salts of succinic acid, more especially as regards their respective solubilities and the conditions for their formation. These results seemed to indicate that the "superacid" salt, $\text{KH}_3(\text{C}_4\text{H}_4\text{O}_4)_2$, is not of the nature of a molecular compound, but that it probably exists in solution and is to be regarded as the salt of a polymerised acid. Seeing that no corresponding salts of other metals have been described, it appeared desirable to investigate more fully the succinates of the other alkali metals in order to discover whether any additional evidence could be obtained from them. The present paper gives the results obtained with the sodium salts, the investigation having been carried out in a manner similar to that adopted for the potassium salts, but over a wider range of temperature.

The crystallised sodium salts described by previous observers are the following: Hexahydrated normal sodium succinate, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot 6\text{H}_2\text{O}$; trihydrated sodium hydrogen succinate, $\text{NaHC}_4\text{H}_4\text{O}_4 \cdot 3\text{H}_2\text{O}$, and the corresponding anhydrous salt. In the course of the present work no superacid salt whatever was isolated, but all three of the above were easily obtained, and also a monohydrated normal salt, $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$.

Normal Sodium Succinate.

The hexahydrated salt is an ordinary article of commerce, and for some of our work the purchased material was taken and recrystallised; at other times it was prepared from sodium carbonate and succinic acid. In concentrated solution, as with the potassium salt, there is some difficulty in getting a sharp neutralisation point with litmus; but the preparation of the pure substance here presents no difficulties, owing to the less solubility and the non-deliqescence of the sodium compound as compared with the potassium one. Good crystals can be obtained from a solution containing an excess of alkali, and the salt can be easily purified by recrystallisation.

This salt forms triclinic crystals, which are stable in ordinary air, but it undergoes transformation on heating. Determinations of the transition-point were made by the dilatometric method, and the temperature found to be 64.9° . No indication of a further

change was observable on heating up to almost 100° . The transition point in presence of the solid acid salt was also wanted for the solubility diagram, and was similarly determined; it is a degree and a-half lower, namely, 63.4° .

For the purpose of finding the composition of the transformed salt, a quantity of the powdered hexahydrate was pressed in a thin layer between porous plates; these were fitted into a shallow glass dish with ground edges, on which rested a ground glass plate, and the whole was heated for a short period in an oven to a temperature of about 70° . The product was a compact, porous cake, very thoroughly drained, which on analysis gave the following results:

0.2166 gave 0.1708 Na_2SO_4 . $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 = 89.9$.

$\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 \cdot \text{H}_2\text{O}$ requires $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 = 90.0$ per cent.

In view of the thoroughly dry nature of the substance, the above numbers clearly indicate that the product is a monohydrate.

The solubility of the normal salt was determined, not only at the temperatures for the isotherms of the diagram (intervals of 25°), but also at intermediate points, so that an accurate curve for it could be drawn. These results are given later.

Sodium Hydrogen Succinate.

The preparation of the acid salt presents none of the difficulties experienced in the case of the potassium salt. This one was obtained at once by half-neutralising succinic acid with sodium carbonate (or, by taking the calculated quantities of these substances, or of the normal salt and succinic acid) and allowing the resulting solution to crystallise at the ordinary temperature. Under these conditions, therefore, the sodium salt is not within a transformation interval, as the potassium one is. The salt crystallises in fine, large, monoclinic crystals, generally somewhat tabular and thick. The crystals themselves are practically quite colourless, but, as the solvent evaporates, the mother liquor becomes decidedly yellow, even when the purest commercial acid, several times recrystallised, has been used for the preparation. Apparently the succinic acid always contains a small quantity of impurity,* which forms with it a solid solution and therefore cannot be removed by recrystallisation, but is not soluble in the solid sodium salt, at least not to anything like the same extent. By recrystallising

* This observation has also been made by Phelps and Hubbard (*Amer. J. Sci.*, 1907, [iv], 23, 211), who recommend that succinic acid which is intended for use as a standard in acidimetry should be prepared from succinic ester; they found that the ordinary recrystallised acid always contains 0.2–0.3 per cent. of impurity.

the salt, very pure product can be obtained, and the final mother liquors are colourless.

The crystals are moderately stable in air, but in a dry or very slightly warm atmosphere they lose water and become white and opaque, but do not crumble to powder. Rapid transformation and semi-fusion are observed on gently warming a crystal in a test-tube. The transition temperature was determined here, also, by the dilatometric method, and found to be 38.7° ; in presence of solid normal salt this is reduced to 34.9° ; in presence of solid succinic acid it is reduced only to 37.8° . This salt lends itself very well to dilatometric observation, on account of the relatively large volume-change involved in its transformation.

A quantity of the pure hydrated salt was warmed to $40-45^{\circ}$ between porous plates, as described above. The product in this case was much more granular than in that of the normal salt, and evidently had not been quite so completely drained. On analysis it gave the following results:

0.3310 gave, on titration, 0.1345 succinic acid, or 40.65 per cent.

0.2519 gave 0.1240 Na_2SO_4 , corresponding with 56.14 per cent. of sodium succinate. This leaves 3.2 per cent. of water; a monohydrate would require 11.4 per cent. of water.

The acid salt therefore transforms directly into an anhydrous compound.

The properties of sodium hydrogen succinate would seem to render it much more suitable than the ordinary recrystallised acid as a standard in acidimetry. It can evidently be prepared in a decidedly purer state, and it can be obtained quite free from included water by allowing the hydrate to effloresce below its transition point, then powdering, and drying in an evacuated desiccator; the effloresced material is, of course, quite porous, and allows of thorough drying, whilst an anhydrous substance, directly crystallised, is always liable to contain included mother liquor. In this case, further, the degree of purity can be very accurately checked by a simple determination of the sodium as sulphate, using the precaution to be mentioned later.

The acid salt (either hydrated or anhydrous, as the case might be) was found to be stable in contact with its solution at all the temperatures dealt with ($0-75^{\circ}$), so that an ordinary solubility curve could be constructed for it also; this is given later, along with the corresponding ones for the normal salt and for succinic acid.

Solubilities of the Sodium Succinates.

The solubility determinations were carried out on approximately the same lines as in the case of the potassium salts. Suitable

quantities of the various ingredients were enclosed in tubes, which were then shaken for some hours in a thermostat kept at the appropriate temperature, after which quantities of the solution were withdrawn through a filter for analysis. At the higher temperatures at which some of the determinations were carried out in the present instance, it was necessary to use jacketed pipettes for this purpose. The temperatures fixed upon were 0° , 25° , 50° , and 75° . At the two last mentioned, some difficulty was experienced in getting consistent results at some parts of the isotherm referring to sodium hydrogen succinate, and it was at first thought that there might really be breaks in this part of the curve; this subsequently appeared not to be the case, however, since repetition of the determinations indicated that through a certain range the results tended to be erratic. A fairly large number of determinations were therefore made in that region. In order further to test the composition of the solid phase at the succinic acid end of this part of the curve, an indirect analysis was carried out. This was done by making up tubes containing weighed quantities of all the ingredients, these being so chosen that the composition of the solution should correspond with a point near the double point, and that a fair quantity of undissolved solid should remain; on analysing the resulting solution the total quantity of succinic acid and sodium succinate dissolved could be calculated (the total quantity of solvent being known), and the quantity of succinic acid and sodium succinate remaining in the solid phase could be obtained by difference. The results agreed well for the ratio $\text{Na} : \text{H} = 1 : 1$, showing the absence of a superacid salt; the only other reason for the existence of a break in the curve would be the existence of another modification of the anhydrous acid salt.

As a rule, duplicate determinations were made only at double points and when the pure substances were being dealt with; in such cases separate tubes were made up, or a considerable interval of time, with continued agitation, was allowed to elapse before a second sample was drawn from the same tube.

For analysis, two portions of each sample were taken. In one the acid was determined by titration with standard baryta solution, using phenolphthalein as indicator; when much sodium salt was present and little acid, the solution was first diluted so that a sharp end-point might be obtained. The second portion was used for the determination of the sodium as sulphate, by evaporation and ignition with sulphuric acid. In the paper dealing with the potassium salts, it was stated that this method of determining the metal was not very satisfactory, on account of the difficulty caused by frothing and charring. This difficulty has now been entirely

obviated by the simple expedient of using an appropriate quantity of acid, so that there is in each case at least enough to convert the whole of the metal into normal sulphate, and not quite enough to convert it into acid sulphate. The quantity of sodium to be expected in any determination was known approximately, and the quantity of acid for each sample could therefore be calculated roughly, but near enough to fulfil the above conditions. Diluted acid of known concentration (about 1:2) was kept in a burette, and the necessary quantity was run into the platinum dish containing the sample; this caused a precipitation of succinic acid, and on cautious evaporation this acid gradually volatilised without charring, leaving a mixture of sodium sulphate and acid sulphate. This residue easily gave pure normal sulphate on ignition, with or without the addition of ammonium carbonate.

The following tables give the results of the various determinations made at the temperatures already stated, and also (for the pure substances and at the triple points) at the transition temperatures:

Temperature 0°.

No.	Weight of solution.	Weight of Na_2SO_4 .	Na_2Su in 1 gram of solution.	Weight of solution.	C.c. of baryta.	H_2Su in 1 gram of solution.	Mols. to $100\text{H}_2\text{O}$.	
							Na_2Su .	H_2Su .
1	—	—	—	4.365	20.70	0.0268	—	0.420
	—	—	—	2.934	13.85	0.0267	—	0.419
	—	—	—	3.079	14.65	0.0269	—	0.421
2	2.224	0.0630	0.0323	2.351	19.81	0.0476	0.39	0.79
3	3.079	0.1453	0.0538	1.720	17.73	0.0583	0.67	1.00
4	2.457	0.1779	0.0826	2.466	31.10	0.0713	1.09	1.29
	2.267	0.1648	0.0829	2.308	29.07	0.0712	1.09	1.29
5	0.871	0.0662	0.0867	1.400	15.50	0.0626	1.10	1.10
6	2.298	0.1950	0.0968	2.566	21.50	0.0474	1.26	0.84
7	2.864	0.2948	0.1174	2.060	12.70	0.0349	1.54	0.63
8	2.520	0.3452	0.1562	2.529	10.48	0.0234	2.12	0.44
9	1.896	0.3051	0.1835	3.150	10.60	0.0190	2.56	0.36
	2.497	0.4026	0.1838	3.562	12.01	0.0191	2.56	0.36
10	1.656	0.2624	0.1807	3.410	10.10	0.0167	2.50	0.32
11	1.114	0.1745	0.1787	3.989	6.66	0.0094	2.45	0.18
12	2.486	0.3849	0.1766	—	—	—	2.38	—
	2.013	0.3110	0.1763	—	—	—	2.38	—

(100 c.c. of baryta solution correspond with 0.5654 gram of succinic acid.)

Temperature 25°.

1	—	—	—	0.8950	12.20	0.0771	—	1.274
	—	—	—	1.0326	14.08	0.0771	—	1.274
2	0.873	0.0282	0.0368	1.447	26.27	0.1026	0.48	1.82
3	1.230	0.0700	0.0649	1.064	22.54	0.1198	0.88	2.24
4	1.131	0.0891	0.0899	0.888	20.96	0.1335	1.29	2.62
5	1.160	0.1286	0.1264	0.963	26.45	0.1553	1.96	3.30
6	1.392	0.1861	0.1524	1.141	34.14	0.1691	2.50	3.80
	1.246	0.1670	0.1529	1.256	37.50	0.1688	2.50	3.80
7	1.142	0.1600	0.1597	1.089	26.73	0.1383	2.53	3.02
8	1.344	0.1944	0.1650	0.863	18.20	0.1198	2.56	2.56
9	1.244	0.2061	0.1889	1.133	16.85	0.0841	2.89	1.76
10	0.872	0.1736	0.2271	1.397	13.96	0.0565	3.52	1.20

Temperature 25° (*continued*).

No.	Weight of solution.	Weight of Na_2SO_4 .	Na_2Su in 1 gram of solution.	Weight of solution.	C.c. of baryta.	H_2Su in 1 gram of solution.	Mols. to 100 H_2O	
							Na_2Su .	H_2Su .
11	0.883	0.2080	0.2688	1.629	11.80	0.0409	4.33	0.90
	0.634	0.1495	0.2688	2.010	14.50	0.0407	4.33	0.90
12	0.569	0.1330	0.2669	1.836	11.20	0.0346	4.25	0.75
13	0.688	0.1598	0.2650	1.906	8.04	0.0238	4.14	0.51
14	0.884	0.2024	0.2611	1.761	2.65	0.0085	3.97	0.18
15	2.351	0.5332	0.2587	—	—	—	3.88	—
	1.937	0.4393	0.2587	—	—	—	3.88	—

(Baryta solution as above.)

Temperature 34.9°.

(Triple point— $\text{NaHSu}, 3\text{H}_2\text{O} : \text{NaHSu} : \text{Na}_2\text{Su}, 6\text{H}_2\text{O}.$ *)*

0.616	0.1670	0.3092	0.578	4.67	0.0566	5.42	1.36
0.734	0.1975	0.3068	0.701	5.54	0.0554	5.35	1.33

Temperature 37.8°.

(Triple point— $\text{NaHSu}, 3\text{H}_2\text{O} : \text{NaHSu} : \text{H}_2\text{Su}.$ *)*

0.752	0.1290	0.1958	0.742	26.97	0.2546	3.96	7.07
0.782	0.1346	0.1962	0.889	32.30	0.2546	3.97	7.07

Temperature 38.7°.

(Double point— $\text{NaHSu}, 3\text{H}_2\text{O} : \text{NaHSu}.$ *)*

0.708	0.1400	0.2255	0.562	13.20	0.1647	4.11	4.12
0.741	0.1454	0.2240	0.4585	10.74	0.1642	4.07	4.10

(100 c.c. of baryta solution correspond with 0.7010 gram of succinic acid.)

Temperature 50°.

1	—	—	—	0.693	23.38	0.1925	—	3.64
2	2.054	0.1071	0.0595	0.583	23.40	0.1929	—	3.65
3	0.407	0.0366	0.1025	0.844	37.50	0.2533	0.93	4.91
4	0.375	0.0414	0.1260	0.665	31.45	0.2696	1.77	6.00
5	0.787	0.1069	0.1549	0.690	34.75	0.2873	3.09	7.86
6	0.780	0.1296	0.1894	0.521	28.28	0.3098	4.20	9.44
7	0.290	0.0500	0.1965	0.479	26.68	0.3178	4.49	9.99
	1.139	0.1964	0.1966	0.388	21.54	0.3168	4.49	9.94
8	1.061	0.1880	0.2022	0.632	31.82	0.2871	4.40	8.98
9	0.722	0.1311	0.2072	0.322	14.97	0.2651	4.36	7.67
10	1.026	0.1935	0.2150	0.332	13.74	0.2361	4.35	6.56
11	0.520	0.0990	0.2170	0.712	27.43	0.2198	4.28	5.96
12	1.008	0.1991	0.2253	0.578	18.70	0.1844	4.24	4.77
13	0.722	0.1472	0.2326	0.871	25.97	0.1700	4.33	4.34
14	1.041	0.2172	0.2380	1.145	31.27	0.1557	4.36	3.92
15	0.756	0.1693	0.2553	1.166	26.77	0.1309	4.62	3.25
16	0.589	0.1459	0.2828	0.657	10.90	0.0946	5.05	2.32
17	0.695	0.1856	0.3048	0.610	7.90	0.0738	5.45	1.81
18	0.686	0.2222	0.3695	0.823	6.07	0.0421	6.97	1.09
19	0.845	0.2760	0.3728	0.602	4.44	0.0421	7.08	1.09
	0.614	0.2012	0.3738	1.374	10.12	0.0420	7.11	1.10
20	0.682	0.2203	0.3635	0.906	4.58	0.0388	6.79	0.73
21	0.723	0.2325	0.3667	1.062	4.95	0.0266	6.72	0.67
22	3.462	1.1035	0.3637	—	—	—	6.36	—
	0.258	0.0826	0.3650	—	—	—	6.38	—

(100 c.c. of baryta solution correspond with 0.5702 gram of succinic acid.)

Temperature 63.4°.

(Triple point— $\text{Na}_2\text{Su}, 6\text{H}_2\text{O} : \text{Na}_2\text{Su}, \text{H}_2\text{O} : \text{NaHSu}$.)

No.	Weight of solution.	Weight of Na_2SO_4 .	Na_2Su in 1 gram of solution.	Weight of solution.	C.c. of baryta.	H_2Su in 1 gram of solution.	Mols. to 100 H_2O	
							Na_2Su .	H_2Su .
	0.579	0.2181	0.4293	1.049	5.10	0.0366	8.93	1.05
	0.662	0.2492	0.4292	1.887	9.12	0.0363	8.92	1.04

Temperature 64.9°.

(Double point— $\text{Na}_2\text{Su}, 6\text{H}_2\text{O} : \text{Na}_2\text{Su}, \text{H}_2\text{O}$.)

	0.768	0.3063	0.4546	—	—	—	9.26	—
	0.793	0.3157	0.4541	—	—	—	9.25	—

(100 c.c. of baryta solution correspond with 0.7520 gram of succinic acid.)

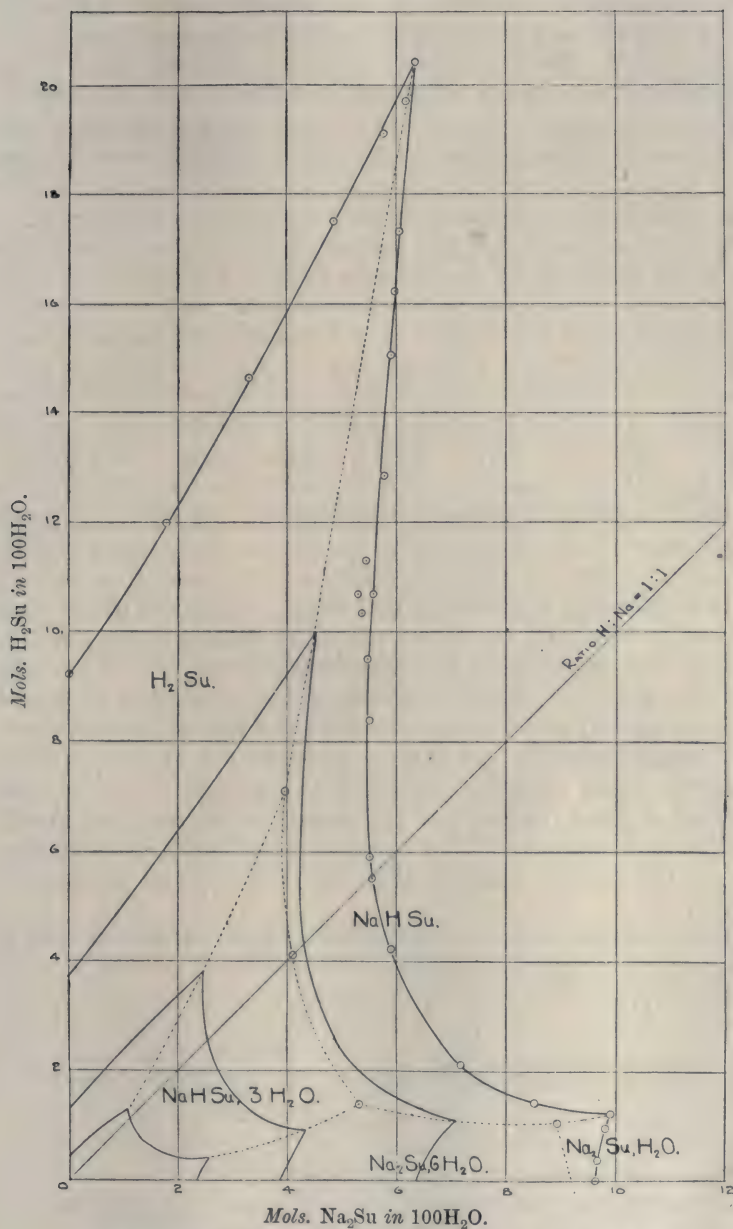
Temperature 75°.

1	{ —	—	—	1.015	50.65	0.3756	—	9.18
	{ —	—	—	0.729	36.56	0.3773	—	9.24
2	1.918	0.1383	0.0822	0.968	52.00	0.4038	1.78	11.99
3	1.574	0.1814	0.1314	1.361	76.90	0.4250	3.29	14.62
4	0.687	0.1020	0.1493	1.564	92.30	0.4438	4.86	17.51
5	1.585	0.2600	0.1871	0.833	50.30	0.4540	5.79	19.30
6	{ 0.677	0.1159	0.1952	1.103	67.50	0.4603	6.30	20.40
	{ 0.896	0.1543	0.1959	0.960	58.60	0.4594	6.31	20.35
7	0.569	0.0974	0.1352	0.737	44.40	0.4532	6.17	19.67
8	1.115	0.1988	0.2035	1.196	67.30	0.4234	6.06	17.32
9	0.436	0.0788	0.2063	0.645	35.10	0.4092	5.96	16.24
10	1.443	0.2670	0.2110	2.277	118.60	0.3918	5.90	15.06
11	0.986	0.1892	0.2188	0.411	19.50	0.3566	5.72	12.82
12	1.068	0.2057	0.2197	1.611	71.05	0.3317	5.44	11.28
13	1.106	0.2208	0.2276	0.800	34.00	0.3195	5.59	10.77
14	0.538	0.1033	0.2191	0.463	19.80	0.3217	5.30	10.69
15	0.867	0.1700	0.2237	0.823	34.26	0.3132	5.37	10.32
16	1.029	0.2100	0.2328	1.850	72.30	0.2940	5.47	9.48
17	1.226	0.2613	0.2430	1.826	65.10	0.2682	5.53	8.37
18	0.941	0.2175	0.2635	0.179	4.87	0.2050	5.51	5.89
19	0.604	0.1426	0.2690	1.036	26.65	0.1934	5.56	5.49
20	0.429	0.1108	0.2945	1.063	21.60	0.1528	5.92	4.22
21	0.912	0.2887	0.3611	1.479	15.32	0.0779	7.15	2.12
22	1.263	0.4570	0.4126	0.290	1.90	0.0493	8.52	1.40
23	{ 1.133	0.4498	0.4530	2.102	11.20	0.0401	9.93	1.20
	{ 1.266	0.5023	0.4525	2.279	12.12	0.0400	9.91	1.20
24	0.360	0.1430	0.4536	1.114	4.70	0.0317	9.80	0.94
25	0.713	0.2870	0.4593	2.298	3.75	0.0123	9.66	0.35
26	{ 0.748	0.3052	0.4653	—	—	—	9.67	—
	{ 0.386	0.1568	0.4632	—	—	—	9.60	—

(Baryta solution as above.)

The results tabulated above are plotted in the diagram, Fig. 1. The actual points are marked only in the case of the isotherm for 75°, for the sake of clearness; the points for the other isotherms lie more consistently on the curves (especially in the case of the acid-salt phase) than do those for 75°.

FIG. 1.



Solubility-diagram for system $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4 : \text{H}_2\text{C}_4\text{H}_4\text{O}_4 : \text{H}_2\text{O}$.
 Isotherms $0^\circ, 25^\circ, 50^\circ, \text{ and } 75^\circ$.

The diagram shows very clearly the stability of the acid salt in contact with its own solution at all the temperatures, although at zero it is not very far removed from its transition interval. On comparing with the diagram for the potassium salt (*loc. cit.*), the most striking features are the greater simplicity due to the absence of a superacid phase, and the very much lower solubility of the normal salt. In the case of the potassium salt, the curve for that phase slopes away very gradually to the extreme right; in the present instance it is inclined abruptly towards the left.

By far the most interesting section of the curves, however, is that which relates to the succinic acid phase. Notwithstanding the non-existence of a solid superacid salt, this part is similar in general nature to that found in the case of potassium; it rises very considerably and more or less steeply, indicating a great increase in the solubility of succinic acid on the addition of sodium succinate. The effect is not the same at all temperatures; on the isotherm for 0° the curve is slightly convex upwards, and rises on the whole at an inclination which is distinctly less than 45° ; on the isotherm for 25° the curve is less convex, and rises at an angle of about 45° ; on the isotherm for 50° it has become slightly concave, and rises at an angle much over 45° , whilst on that for 75° it is distinctly concave and still steeper. At some temperature between 25° and 50° the curve would be practically straight, so that at this temperature the increased amount of succinic acid dissolved would be simply proportional to the amount of sodium succinate added; above this temperature the rate of increase would grow with increase in the sodium concentration; below, it would diminish. Here, also, the increase in the amount of succinic acid dissolved for each molecule of sodium salt added increases greatly with rise of temperature. For rough purposes this may be brought out by the method used in the case of the potassium salt, as follows:

The molar concentration (per 100 mols. H_2O) of succinic acid in saturated pure aqueous solution is:

At 0° .	25° .	50° .	75° .
0.42	1.27	3.64	9.21

In presence of sodium succinate the maximum (first double point) is:

1.29	3.80	9.96	20.37
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The respective increases are therefore:

0.87	2.53	6.32	11.16
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The sodium succinate concentrations at these points are:

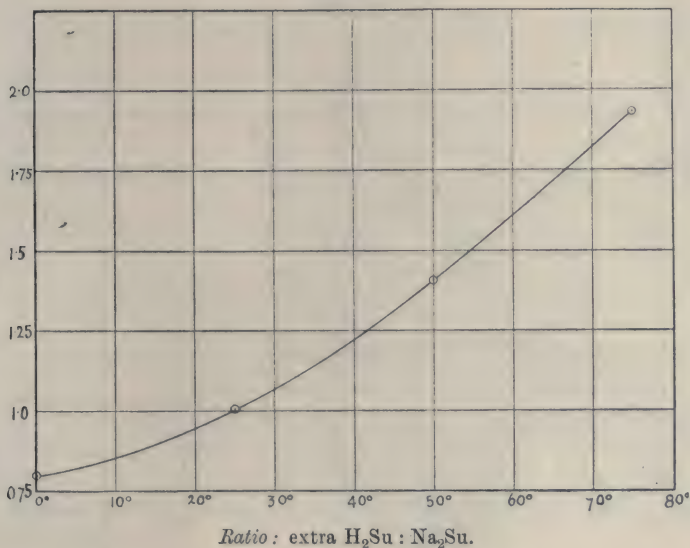
1.09	2.50	4.49	6.30
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Dividing these numbers into the preceding ones, this gives for the ratio—*extra* $\text{H}_2\text{Su} : \text{Na}_2\text{Su}$:

At 0°.	25°.	50°.	75°.
0.80	1.01	1.41	1.93

It will be observed that at 75° the addition of sodium succinate brings about the dissolution of about twice its equivalent of succinic acid, so that the increase cannot be explained as due merely to the formation of the ordinary acid salt, and it seems most probable that sodium also forms a superacid salt in solution, but

FIG. 2.

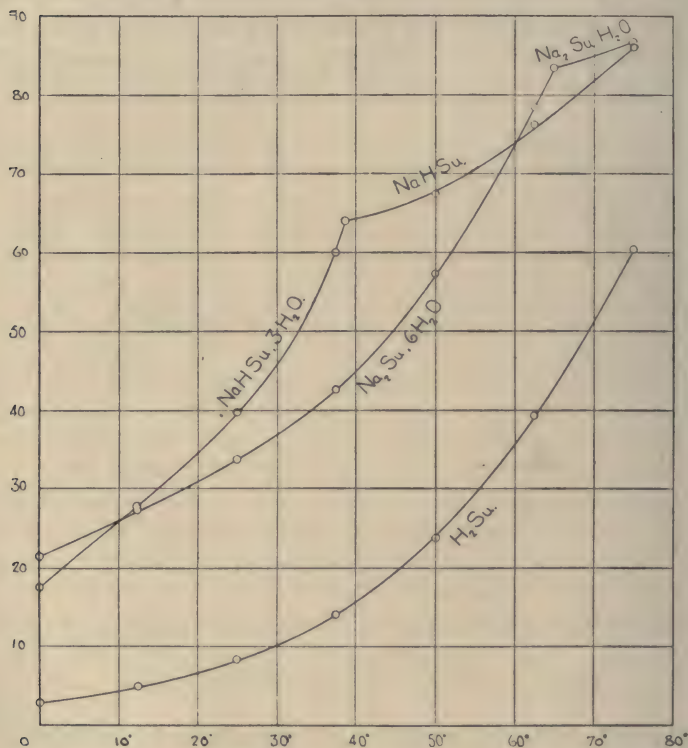


that this salt cannot be separated, on account of its solubility being greater than that of the ordinary acid salt and of the free acid.

If the ratios above deduced are plotted against the temperatures, they give the curve shown in Fig. 2. Assuming the above explanation (the formation of superacid in solution), it would be expected that the curve should tend towards a maximum value; this value would be 3 if the sodium salt were analogous to the known potassium one. Although the curve shows no clear indication of a tendency towards such a maximum, its nature is such as to leave the possibility quite open. The ratios for the effect produced by the addition of potassium succinate, given in the previous communication, do not show such a regular gradation, and may possibly require revision as well as extension; for corresponding tem-

peratures, however, the values lie well above those for sodium. It is intended to compare the effects produced by other alkali-metal succinates; preliminary results indicate that the increase of solubility (or of polymerisation effect) is greater for rubidium than for potassium, and still greater for caesium, so that

FIG. 3.



Solubility-curves for sodium succinate, sodium hydrogen succinate, and succinic acid.
(Grams of anhydrous substance in 100 grams of water.)

it apparently increases with the electropositive character of the metal.

As already mentioned, it was considered desirable to prepare, for ordinary purposes, solubility curves for succinic acid, sodium hydrogen succinate, and normal sodium succinate. For this purpose additional determinations were made at temperatures midway between those of the isotherms; the combined results, stated in

grams of anhydrous solute per 100 grams of water, are given in the following table and plotted in the curves, Fig. 3:

	0°.	12·5°.	25°.	37·5°.	38·7°.	50°.	62·5°.	64·9°.	75°.
Na ₂ Su	21·45	27·38	34·90	43·64	—	56·30	78·49	83·38	86·63
NaHSu ...	17·55	27·93	39·82	60·01	63·99	67·37	76·15	—	86·00
H ₂ Su	2·75	4·92	8·35	14·10	—	23·83	39·35	—	60·37

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LXXXIX.—*The Constitution and Synthesis of Caoutchouc.*

By SAMUEL SHROWDER PICKLES.

THE first mention of the polymerisation of isoprene was made by Williams in 1860 (*Proc. Roy. Soc.*, 1860, **10**, 517), who observed that isoprene, when left in a bottle for some months, became sticky, lost its fluidity, and became "ozonised" * by absorbing the oxygen of the air. On careful distillation of this sticky product, some isoprene first passed over; the temperature then rose quickly, and the residue was converted into a white, spongy mass, which gave on analysis figures agreeing with the formula $C_{10}H_{16}O$.

Bouchardat (*Compt. rend.*, 1879, **89**, 1117) afterwards observed that when isoprene was heated in a sealed tube with carbon dioxide at 280—290° for ten hours, it was converted into a viscous, sticky mass, consisting of isoprene, a terpene ($C_{10}H_{16}$) or terpenes, and higher boiling products. Bouchardat also was the first to state that on treating isoprene with cold aqueous hydrochloric acid an elastic polymeride was produced, which, after boiling with water, possessed the properties of india-rubber.

In 1882 Tilden (*Chem. News*, 1882, **46**, 120; *Brit. Assoc. Report*, 1882) obtained this elastic polymeride with isoprene produced from turpentine oil. On treatment with concentrated hydrochloric acid, he obtained a tough, elastic product, closely resembling caoutchouc. He also obtained an elastic polymeride by treating isoprene with nitrosyl chloride.

In 1887 Wallach observed that on allowing isoprene to remain exposed to light in a sealed tube for a long time, it underwent a change, and, on subsequently adding alcohol to the liquid, there separated a tough, indiarubber-like mass, which, on keeping in the air for some time, resinified.

* Auto-oxidation, not to be confounded with the action of ozone as nowadays understood.

In May, 1902, Tilden recorded his observations on the spontaneous conversion of isoprene (obtained from turpentine) into indiarubber. Specimens of isoprene which had been kept in bottles for some considerable time were found to have become converted into masses of a solid of a yellow colour. This turned out to be caoutchouc. A solution in benzene left, on evaporation, a residue agreeing in all characters with a similar preparation from Para rubber.

The spontaneous polymerisation of isoprene was also afterwards observed by Weber in 1894 (*J. Soc. Chem. Ind.*, 1894, 13, 11).

Concerning the results of Tilden, a certain amount of scepticism has been expressed, or suggested, in recent times, first by Klages at Heidelberg, and latterly by Harries in a lecture delivered in Vienna (*Chem. Zeit.*, 1910, 34, 316), the first with regard to the possibility of converting isoprene into rubber by the processes mentioned by Tilden, and the second questioning the identity, with caoutchouc, of the material obtained. Harries stated, after examining in November, 1909, a sample of rubber said to be obtained by the process of Dr. Fritz Hoffmann, that he was convinced hereby, for the first time, that synthetical caoutchouc had been produced. The nature of the process was not stated, but shortly afterwards Harries himself discovered a method for converting isoprene into caoutchouc, namely, by heating it to somewhat above 100° with glacial acetic acid in a sealed tube.

Spontaneous Polymerisation of Isoprene and Examination of the Product.

In view of the position of the subject at the present time, the author considered that an account of the result of a recent experiment on the polymerisation of isoprene might have some little value, especially as chemical tests were applied to the product obtained. The difficulty, so far as repetition is concerned, lies in the fact that the process of spontaneous polymerisation is an extremely slow one, the complete conversion requiring several years.

On the occasion of submitting a report on "The Position of the Chemistry of Rubber" to the Chemical Section of the British Association in 1906, the author prepared a specimen of isoprene (about 10 grams) for demonstration purposes.* The small bottle containing it was almost full, the stopper was securely fastened down, and the specimen was allowed to remain in that condition (for the greater part of the time in the dark) for three and a-half years. The liquid, which at first was as mobile as ether, had during this period gradually become more viscous, until it acquired the consistency of a thick syrup. A short time ago a portion of this liquid was poured out, and to it

* The isoprene (boiling at 35–37°) was prepared from plantation biscuit rubber.

was added about 10 volumes of alcohol. The separation of a white substance, followed by a clotting, took place immediately. The coagulum thus formed was washed with alcohol and allowed to dry on a glass plate. As thus prepared, the material was clear, gelatinous, and possessed of a certain amount of elasticity. In point of tenacity, however, it was certainly not equal to mature Para rubber, but rather resembled the product obtained from young, immature rubber trees. It should be remembered, however, that in the experiment the polymerisation had not been allowed to proceed to completion, that is, until reaching the completely solid state. That the material undoubtedly contains rubber, however, is proved by the fact that it yields the characteristic tetrabromide and the nitrosite.

On adding chloroform to a portion of the polymeride, it exhibited to a certain extent the swelling so noticeable in the case of natural rubber, and then gradually passed into solution. The liquid was cooled, and bromine (in chloroform solution) was added gradually until the red colour remained. The chloroform solution was then poured into an equal volume of alcohol, when the characteristic, white, fibrous caoutchouc tetrabromide separated at once.

Another portion of the substance was dissolved in benzene, and nitrous gases, obtained from nitric acid and arsenious oxide, were passed into the solution. In this case, also, the behaviour was just as in the case of natural rubber. A yellow, gelatinous material first separated from the solution. The contents of the flask were kept for several hours, and, on then removing the precipitate, it was obtained as a yellow, amorphous powder similar in properties and in general behaviour to the product known as caoutchouc nitrosite obtained by similarly treating natural rubber.

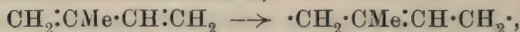
Both these tests are regarded at the present time as characteristic of rubber (or gutta-percha, which yields similar compounds). There is also another test, namely, the preparation of the ozonide and its subsequent decomposition into lævulinaldehyde and lævulic acid, but the author has not been able to apply this owing to the small amount of material at his disposal.

The Formation and Constitution of Caoutchouc.

The author wishes to take this opportunity of putting forward a view of the mode of formation of caoutchouc and of its possible constitution. This suggestion was first made at the British Association at York, in 1906, in the discussion on Tilden's paper, but as the discussion was not printed, the suggestion has not been previously published.

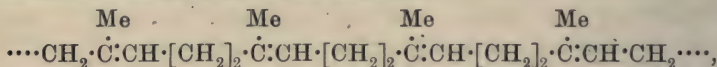
Since Harries has shown that lævulinaldehyde, lævulinaldehyde

peroxide, and lævulic acid are the only oxidation products of caoutchouc, the polymerisation of isoprene into rubber must be accompanied by a rearrangement of the double bonds,



as on no other assumption is the formation of lævulinaldehyde possible.

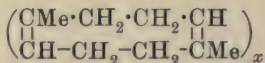
As is well-known, this re-arrangement takes place in many cases where substances possessing conjugated ethylenic linkings enter into chemical combination. It is suggested that these unsaturated C_5H_8 nuclei unite to form long chains of the structure :



and that the number of C_5H_8 complexes may vary in different kinds of rubber, the difference in properties being probably due to this variation in the number of complexes contained. The oxidation results require that the two ends of the chain should be linked together, which, of course, leads to the formation of a ring, but it is proposed that in each rubber molecule there is only one such ring. Rubber probably contains at least eight C_5H_8 complexes connected as above indicated.

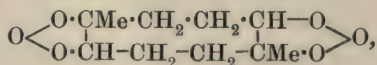
This suggestion is put forward as an alternative to Professor Harries' *cyclooctadiene* formula, which is to a certain extent unsatisfactory, as its arrangement demands the employment of vague and unnecessary conceptions of polymerisation.

The formula for caoutchouc put forward by Harries is the following :



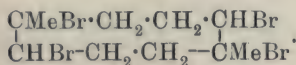
The single molecule is regarded as the "chemical" molecule, and the polymerised aggregate as the "physical" molecule. The extent of polymerisation (x) is undefined.

The following are the principal reasons given for the adoption of this formula : When treated with ozone, rubber yields an ozonide having the empirical composition $\text{C}_{10}\text{H}_{16}\text{O}_6$, which, when acted on by water, decomposes, giving as the only products of decomposition, lævulinaldehyde, lævulinaldehyde peroxide, and lævulic acid. The molecular weight of the ozonide as first determined was stated to be 526 (*Ber.*, 1904, 37, 2709). On subsequent determination (*Ber.*, 1905, 38, 1195), however, Harries found the molecular weight to be in accordance with the formula $\text{C}_{10}\text{H}_{16}\text{O}_6$. Harries therefore considered the formula of the ozonide to be :



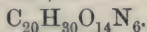
the disruption on treatment with water taking place between the carbon atoms previously connected by the double bond. Consequently, the individual molecule of caoutchouc would have the single dimethyl-*cyclooctadiene* formula.

For this view of the composition of caoutchouc the assumption is necessary that the polymerisation is either purely physical or that the connexion between the individual chemical molecules is of so loose a nature as to allow the ozone first to depolymerise the aggregate before it attaches itself to the individual molecules. The necessity for this rather vague and unsatisfactory assumption results from the acceptance of the dimethyl-*cyclooctadiene* formula, for if the polymerisation were chemical in character, the polymeride formed would be relatively less unsaturated than the $C_{10}H_{16}$ nucleus. This, however, is not the case, for rubber contains one ethylenic linking for every C_5H_8 complex. Moreover, there are several facts which are not satisfactorily explained by Harries' formula. Since ozone effects depolymerisation, it is to be expected that other substances which tend to saturate the compound will likewise have a similar primary influence. Bromine should therefore first depolymerise the colloidal molecule, and then form simple molecules having the formula



But the properties of the bromo-derivative of caoutchouc and its general behaviour indicate a composition probably as complex as that of caoutchouc itself.

Similarly, nitrous gases might be expected to act in the same manner as ozone, yet Harries has shown that, by their action on rubber, compounds are formed having formulæ (confirmed by molecular-weight determinations) such as $C_{40}H_{62}O_{24}N_{10}$ and



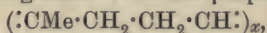
In a case of physical polymerisation, heat might be expected to resolve the polymeride into simple $C_{10}H_{16}$ molecules. If, however, rubber is heated under atmospheric pressure the result is, in all respects, like that of a complex compound undergoing complete disruption, whilst if, on the other hand, the treatment is applied more gently (for example, distillation in a vacuum), the smallest molecules obtained in the distillate probably contain at least twenty carbon atoms.

Further, although it might be conceived that an unsaturated compound could undergo polymerisation, due perhaps to the exertion of labile valencies, it is contrary to chemical experience that saturated compounds should do so. Therefore, on reduction one should get simple $C_{10}H_{20}$ molecules if Harries' formula is the correct

one. Such a hydrocarbon would probably boil about 170° . Berthelot (*Bull. Soc. chim.*, 1869, [ii], 11, 33) found, however, that on reducing caoutchouc by heating it to high temperatures with hydriodic acid, hydrocarbons of the paraffin series were produced, which boiled above 350° .

Or, reverting again to the bromine compound, if rubber is a chemical polymeride consisting of octa-carbocyclic nuclei linked together, then on treatment with bromine it should either (1) remain in the polymerised form and absorb only two atoms of bromine for each $C_{10}H_{16}$ group, or (2) become depolymerised and give simple $C_{10}H_{16}Br_4$ molecules; but it does neither, it absorbs four atoms of bromine and remains a complex molecule.

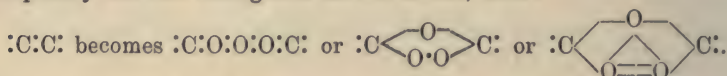
In the case of the long-chain formula proposed:



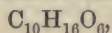
the polymerisation is regarded as being strictly chemical.

The Constitution of Caoutchouc Ozonide.

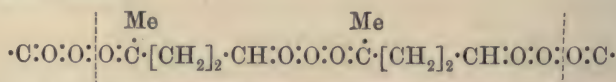
The behaviour of the ozonide can perhaps be best accounted for by assuming that ozone, in acting on an unsaturated compound, separates completely the two contiguous carbon atoms, thus:



A series of such linkings occurring in a long chain would probably be readily resolvable by water, and even in the absence of water would be a source of weakness. Thus, on distillation or heating in solution, the portion of the ozonide capable of holding together might be



as indicated below:



The whole chain (provided it contained an even number of C_5H_8 complexes) could thus break up into $C_{10}H_{16}O_6$ molecules, which, on treatment with water, would yield lævulinaldehyde, etc.

In some cases three or more $C_5H_8O_3$ complexes might hold together, and the manner of their disruption on hydrolysis determine the proportions of aldehyde, peroxide, and acid produced.

XC.—*The Effect of Contiguous Unsaturated Groups on Optical Activity. Part V. Physico-chemical Evidence of the Structure of "α-Disulphoxides."*

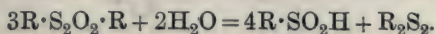
By THOMAS PERCY HILDITCH (1851 Exhibition Scholar).

THE results of investigating the general effect of various constitutive features on optical activity (some of which have been communicated in earlier parts of this series) have shown that, although in some cases the constitutive influence is too indefinite to produce an invariably well-marked change, in others a definite qualitative alteration in the magnitude of the rotatory power follows the structural change concerned. This is to be remarked especially in the effects produced by two adjacent unsaturated groups, and, also, in a molecule (containing either one or two such conjugated radicles) completely symmetrical about the centre of the unsaturated systems present (Trans., 1908, **93**, 1618; 1909, **95**, 1570). The latter arrangement, indeed, would appear to be the most favourable of any to a large anomaly in rotatory power, in the light of certain additional data shortly to be published.

In the meantime it is well to inquire whether the better-defined influences to which reference has been made are such as to permit the use of optical activity, by reason of its susceptibility to structural changes, as an occasional physico-chemical aid in elucidating questions of uncertain molecular structure.

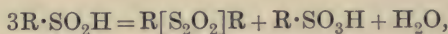
Thus, for example, the author has pointed out (Trans., 1908, **93**, 1622) that the rotatory powers of alkaloid salts of aromatic sulphinic acids accord better with the formula $R \cdot SO_2 \cdot X$ than with $R \cdot SO \cdot OX$, thus confirming from a physical point of view the structure usually assigned to such salts on account of their chemical behaviour.

A more interesting case, not yet definitely settled from chemical evidence, is that of the "α-disulphoxides," to which the formulæ $R \cdot SO \cdot SO \cdot R$ and $R \cdot SO_2 \cdot SR$ have both been assigned at different times. These compounds, which are formed in the oxidation of mercaptans, in the auto-oxidation of sulphinic acids, and by synthesis from alkyl iodides and sodium alkylthiosulphonates, were regarded by Otto (*Ber.*, 1882, **15**, 121, etc.) as alkylthiosulphonic esters on account of the last-mentioned synthesis and of certain decomposition reactions, notably their behaviour on warming with aqueous alkali, when a mixture of sulphinate and disulphide results:

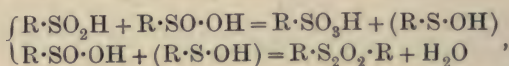


More recently, the transpositions of a number of organic sulphur compounds have been explained by the supposed intermediate formation of a hypothetical "sulphoxylic acid," $R \cdot S^{IV} \cdot OH$ (the bivalent sulphur analogue of sulphinic and sulphonic acids); admitting the possibility of this acid occurring as an intermediate phase in the decomposition of " α -disulphoxides," the reactions from which Otto deduced the thiosulphonic formula may all be equally well interpreted by the symmetrical alternative, $R \cdot SO \cdot SO \cdot R$.

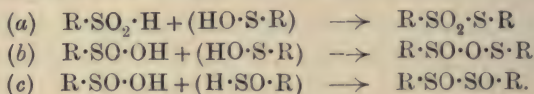
Moreover, Fromm and Seixas Palma (*Ber.*, 1906, **39**, 3308), discussing the reaction:



have shown that it may take place in two stages:



and that the latter condensation may occur in either of three ways:



Experimental evidence was then brought forward in favour of the last reaction (c).

Finally, Hinsberg (*Ber.*, 1908, **41**, 2836, 4294) has observed the easy reduction of di- β -naphthyl "disulphoxide" to the disulphide by hydriodic acid in glacial acetic acid at the ordinary temperature, such ease being inconsistent with the presence of a sulphone radicle.

This by no means exhausts the reactions (both of formation and of decomposition) of these compounds, which have received attention from previous workers, but the only definite chemical evidence pointing clearly to one or other of the two alternative formulæ is practically summed up by (i) the action between sodium alkylthiosulphonates and alkyl iodides (in favour of $R \cdot SO_2 \cdot S \cdot R$) and (ii) the easy reduction of di- β -naphthyl disulphoxide (Hinsberg), and Fromm and Seixas Palma's experiments on dibenzyl disulphoxide (*loc. cit.*) (in favour of $R \cdot SO \cdot SO \cdot R$).

Now, it is readily seen that whilst the true α -disulphoxide formula, $R \cdot SO \cdot SO \cdot R$, contains a conjugated system of two unsaturated groups, about the centre of which the entire molecule is symmetrical, the alternative thiosulphonic structure, $R \cdot SO_2 \cdot SR$, is non-symmetrical, and contains the relatively saturated sulphone radicle combined with the less saturated bivalent sulphur residue. Consequently, fresh evidence might be hoped for from a study of disulphoxides in which the alkyl radicles R were optically active. Unfortunately, only one optically active sulphinic acid is known at

present, and the observations now submitted are therefore restricted to this one instance—that of camphor β -thio-derivatives.

Before describing the experiments undertaken, it will be necessary to give a summary of the data in this series available for use as a basis of comparison (in calculating the differences per camphoryl radicle in the table, the general effect of unsaturation on the camphoryl group has been reckoned as positive)*:

	[M] _D .	Difference.
Camphor, C ₁₀ H ₁₆ O	+ 67·2	—
<i>Sulphur atom relatively saturated :</i>		
{ Camphor- β -sulphonic acid, C ₁₀ H ₁₅ O·SO ₃ H	+ 49·0	+ 18·2
{ ,, chloride, C ₁₀ H ₁₅ O·SO ₂ Cl	+ 78·0	- 10·8
<i>Sulphur atom saturated ; molecule symmetrical :</i>		
Dicamphoryl- β - α -disulphone, C ₁₀ H ₁₅ O·SO ₂ ·SO ₂ ·C ₁₀ H ₁₅ O	+ 131·6	+ 1·4
<i>Sulphur atom unsaturated :</i>		
Camphoryl- β -mercaptan, C ₁₀ H ₁₅ O·SH	+ 11·0	+ 56·2
<i>Sulphur atom unsaturated and adjacent to a second unsaturated group :</i>		
{ Camphoryl- β -mercaptan acetate, C ₁₀ H ₁₅ O·S·CO·Me ...	- 93·0	+ 160·2
{ ,, benzoate, C ₁₀ H ₁₅ O·S·CO·Ph...	- 46·0	+ 113·2
<i>Sulphur atom unsaturated and adjacent to another unsaturated sulphur atom ; molecule symmetrical :</i>		
Dicamphoryl β -disulphide, C ₁₀ H ₁₅ O·S·S·C ₁₀ H ₁₅ O	- 355·0	+ 244·7

The series therefore appears well-suited for distinguishing between formulæ involving symmetrical conjugation on the one hand, and non-symmetrical simple unsaturation on the other.

Dicamphoryl β - α -disulphoxide was found to be readily obtainable from camphor- β -sulphinic acid (Smiles and Hilditch, *loc. cit.*) under the conditions described in the experimental part of this paper ; it was examined in the polariscope in a number of solvents (neutral, acidic, and alkaline), with the following results :

Solvent.	Percentage concentration.	Temp.	[α] _D .	[M] _D .
Chloroform { at once.....	5·0	16·5°	- 64·72	- 257·5
,, { after 18 hours.....	—	16·5	64·68	257·4
,, { immediately	1·0	16·5	68·80	273·8
Alcohol ,,	1·0	16·5	65·20	259·5
Alcoholic hydrogen { immediately	1·0	17·5	55·10	219·4
chloride (dilute). { after 30 hours.....	—	17·0	56·10	223·3
,, { 21 days	—	17·5	52·40	208·6
Glacial acetic acid, immediately	1·0	20·0	58·60	233·2
Alcoholic sodium ethoxide (dilute)....	1·0	22·0	51·40	204·6

In the last instance, decomposition rapidly set in, and a film of crystals deposited on the tube invariably prevented continued readings.

* These data have been collected from the work of Reychler (*Bull. Soc. chim.*, 1898, [iii], 19, 120) ; Armstrong and Lowry (*Trans.*, 1902, 81, 1447) ; Smiles and Hilditch (*Trans.*, 1907, 91, 519) ; Lowry and Donington (*Trans.*, 1903, 83, 479).

These numbers indicate very plainly the presence of a strong constitutive influence on the rotatory power, or, in other words, are in favour of the symmetrical structure, $C_{10}H_{15}O \cdot SO \cdot SO \cdot C_{10}H_{15}O$.

Other derivatives, in which one camphoryl radicle is replaced by other groups, have been found, however, to furnish somewhat varying results. Thus, *sodium camphor-β-thiosulphonate* was prepared from camphor β-sulphonyl chloride by warming it with alcoholic sodium sulphide, and from this, by the action of the respective alkyl iodides dissolved in their corresponding alcohols, *camphoryl-, methyl-, and n-butyl-β-disulphoxides* were isolated in the solid state; the preparation of the *ethyl* and *n-propyl* compounds was also attempted, but these substances were found to be of an oily, non-crystalline nature. The further polarimetric data obtained were as follows:

Substance.	Solvent.		Percent- age con- centration.	Temp.	[α] _D .	[M] _D .
Sodium camphor-β-thiosulphonate :						
	Water		5·0	16·5°	+11·52	+31·1
Camphoryl methyl-β-disulphoxide :						
	Chloroform (at once).....		2·5	16·5	45·44	119·1
	" (after 18 hours).		—	16·5	44·48	116·5
	Alcoholic hydrogen chloride (dilute)	{ (at once) (after 18 hours). —	1·0 —	22·0 22·0	34·60 29·50	90·7 77·3
	Alcoholic sodium ethoxide (dilute)	{ (at once) (after 18 hours). —	1·0 —	22·0 22·0	-2·90 -6·10	-7·6 -16·0
Camphoryl n-butyl-β-disulphoxide :						
	Chloroform (at once)		1·0	17·0	-23·60	-71·7

The alkaline solution of the methyl derivative possessed, almost from the commencement, the characteristic odours of methyl mercaptan and disulphide.

For comparison with the original table of camphor β -thio-derivatives (p. 1093), the values of the molecular rotatory powers of the compounds under discussion, together with their differences from that of camphor itself, are collected below:

	Camphoryl methyl- β -		Camphoryl <i>n</i> -butyl- β -		Dicamphoryl- β -		[M] _D	Diff.
	[M] _D	Diff.	[M] _D	Diff.	[M] _D	Diff.		
Sodium camphoryl- β -thiosulphonate (aqueous solution) ...							+31.1	+36.1
Disulphoxides :								
In chloroform	+116.5	-49.3	-71.7	+138.9	-273.8	+204.1		
In alcoholic HCl ...	+77.3	-10.1	—	—	-219.4	+176.9		
In alcoholic NaOEt.	-16.0	+83.2	—	—	-204.6	+169.5		

The optical data therefore indicate that, whilst the compound containing two identical "alkyl" groups undoubtedly

exists in the symmetrical form $R \cdot SO \cdot SO \cdot R$, the structure varies when the groups R , R^I in $R \cdot S_2O_2 \cdot R^I$ are not the same. It appears that when these differ widely in nature or mass ($R \cdot SO_2 \cdot SNa$ or $R \cdot SO_2 \cdot S \cdot Me$), the compound in question exists entirely in the thio-sulphonic form; the *n*-butyl derivative, on the other hand, is a case where R^I is approaching R in mass, and would appear, from its rotatory power, to be already in the conjugated form $R \cdot SO \cdot SO \cdot R^I$.

It will be noticed that, interpreting the results thus, no explanation is forthcoming of:

- (i) the non-existence of transitional or isomeric forms.
- (ii) the formation of symmetrical derivatives in the action of alkyl iodides on sodium alkylthiosulphonates.

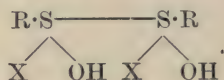
Relatively little attention has hitherto been paid to any but the symmetrical disulphoxides, $R \cdot S_2O_2 \cdot R$; several attempts were made to isolate a definite isomeric form of dicamphoryl β -disulphoxide, but all failed (compare Hinsberg, *loc. cit.*). It is, moreover, possible that the non-crystalline nature of the ethyl and *n*-propyl compounds may be due to the presence of a mixture of isomerides.

The second difficulty, on the other hand, can be explained as a matter of isomeric rearrangement to the more stable form; this conception appears preferable, in view of the general reactions of metallic alkylthiosulphonates and of the rotatory power of sodium camphor- β -thiosulphonate, to the adoption of a formula $R \cdot SO \cdot SONa$ for the latter, put forward by Gutmann (*Ber.*, 1908, **41**, 3351).

Returning for a moment to the values of rotatory power observed, it will be noticed that acetic acid, dilute hydrochloric acid, and dilute alcoholic alkali diminish the lævorotation of the dicamphoryl compound, but also depress the dextrorotation of the methylcamphoryl derivative. In the last instance, as shown later, this phenomenon is probably connected with the decomposition which occurs; but in the case of the acids this does not apply, since the amount of reaction which occurred on heating a solution of dicamphoryl β -disulphoxide at 100° with alcoholic hydrogen chloride was small. The greater part of the compound was subsequently recovered, although it was not quite pure; since, however, di-*p*-tolyl disulphoxide is quite unaltered by similar treatment, it is probable that in the former case, as well as in the preparation of the former derivative by heating with dilute acid, the impurity is a small quantity of by-product difficultly removable by recrystallisation rather than an isomeric form of the disulphoxide.

On the other hand, the dicamphoryl and di-*p*-tolyl compounds both dissolve in alcoholic hydrogen chloride to a yellow solution,

and with a slight, but quite perceptible, evolution of heat. The solution in glacial acetic acid, also, is faintly yellow. This may well be regarded, in view of the known basic character of the sulphoxide group, as being due to partial "salt-formation":



It may be mentioned that Hinsberg (*Ber.*, 1909, **42**, 1278) has observed examples of two symmetrical disulphoxides, which crystallise with two molecules of acetic acid.

The change in optical activity in presence of acid solvents agrees in all the observed cases with the assumption of a partial formation of sulphoxide salts.

EXPERIMENTAL.

The camphor- β -sulphinic acid used was prepared by adding camphor- β -sulphonyl chloride, dissolved in a little boiling acetone, to a strong aqueous solution of about double the theoretical quantity of sodium sulphite heated at 100°, the mixture being finally boiled until it was perfectly clear. Under the most favourable conditions, yields of more than 90 per cent. were thus obtained; the resulting acid, which melted at 63–64° and had $[\alpha]_D^{20} -74.50^\circ$ in 2 per cent. aqueous solution, was in all respects identical with that prepared by reduction of the chloride with zinc dust (Smiles and Hilditch, *loc. cit.*).

The transformation to the disulphoxide was first effected by leaving an aqueous suspension of the acid (in presence of a little dilute sulphuric acid) on the steam-bath for a week; the oily product was made alkaline in the cold, when it at once solidified, and, after one recrystallisation from light petroleum, melted at 183°. Four more recrystallisations raised the melting point to 212°, when it remained unaltered by further purification. It was observed later that the presence of traces of hydriodic acid materially accelerated the reaction, the maximum yield being attained in a few hours instead of days, and the product being much more pure. Moreover, an attempt made to prepare camphor- β -sulphonyl iodide from the sodium sulphinate and iodine in aqueous solution gave as its only result a quantity of the disulphoxide.

On the other hand, the usually good method of heating the aqueous sulphinic acid in sealed tubes at 130° failed to give a pure product.

Dicamphoryl β - α -disulphoxide forms colourless, highly refracting prisms, very readily soluble in alcohol, benzene, chloroform, or

acetic acid, less so in boiling, and almost insoluble in cold light petroleum, and melting at 212° :

0.1047 gave 0.2302 CO_2 and 0.0685 H_2O . $\text{C}=59.96$; $\text{H}=7.27$.

0.1717 „ 0.2024 BaSO_4 . $\text{S}=16.19$.

0.2098, in 13.39 benzene, gave $\Delta t = -0.180^{\circ}$. $\text{M.W.}=426.5$.

$\text{C}_{20}\text{H}_{30}\text{O}_4\text{S}_2$ requires $\text{C}=60.30$; $\text{H}=7.53$; $\text{S}=16.08$ per cent.

$\text{M.W.}=398$.

The compound was found to be analogous to the true aromatic or fatty disulphoxides hitherto described. Thus, on warming with dilute aqueous sodium hydroxide at 100° for an hour, decomposition took place. The white insoluble product was recrystallised from alcohol, and then melted at $221-222^{\circ}$, whilst 0.1092, made up to 10 c.c. with dry chloroform, gave $[\alpha]_{\text{D}}^{20} - 93.04^{\circ}$. (Found, $\text{C}=64.86$; $\text{H}=8.52$.)

Dicamphoryl β -disulphide melts at 224° , has $[\alpha]_{\text{D}} - 97^{\circ}$, and requires $\text{C}=65.57$; $\text{H}=8.19$ per cent.

The aqueous alkaline filtrates were saturated with carbon dioxide, evaporated to dryness at 100° , and twice extracted with boiling alcohol. The crystalline sodium salt obtained, dissolved in concentrated sulphuric acid, gave a characteristic deep blue colour on addition of a drop of phenetole, and was evidently sodium camphor- β -sulphinic acid, the alkaline decomposition having thus pursued the usual course.

It has been already mentioned that similar treatment with dilute alcoholic hydrogen chloride had little effect. Analysis of the recovered product gave the following numbers:

0.1802 gave 0.4022 CO_2 and 0.1266 H_2O . $\text{C}=60.86$; $\text{H}=7.81$.

$\text{C}_{20}\text{H}_{30}\text{O}_4\text{S}_2$ requires $\text{C}=60.30$; $\text{H}=7.53$ per cent.

It was thought that oxidation of disulphoxides in cold glacial acetic acid by powdered potassium permanganate might lead to a new synthesis of α -disulphones, especially as the latter compounds result, together with sulphonic acids, in the similar oxidation of sulphinic acids (Trans., 1908, **93**, 1524). From di-*p*-tolyl or di- β -naphthyl disulphoxides, however, as well as from the camphor derivative, nothing but the sulphonic acid was thus obtained. In the latter case, the acid product was isolated in the form of its potassium salt, which was then converted into the sulphonyl chloride in the usual way. The latter, after crystallisation from light petroleum, melted at $66-68^{\circ}$, and had $[\alpha]_{\text{D}}^{20} + 30.60^{\circ}$ in 1 per cent. chloroform solution. Since the only two known methods of formation of α -disulphones apparently depend on the presence of the desmotropic sexavalent sulphinic acid form, this result may be regarded as an indication of the absence of any sulphone nucleus in the symmetrical disulphoxides studied.

Sodium camphor- β -thiosulphonate, $C_{10}H_{15}O \cdot SO_2 \cdot SNa$, was readily prepared by acting on camphor- β -sulphonyl chloride with sodium sulphide, and was obtained in yields nearly equal in weight to that of the sulphonyl chloride used. To a solution of 10 grams of pure sodium sulphide, in about 20 c.c. of alcohol, an equal weight of the sulphonyl chloride dissolved in the same bulk of alcohol was added in very small quantities at a time, no fresh addition being made until all the sulphur, which is temporarily set free during the reaction, had been reabsorbed. The mixture was finally boiled for a short time, and, to remove certain by-products which are always encountered, was then filtered and, when cold, poured into water. The solution was extracted with benzene, and the aqueous layer evaporated. For analysis, the salt was purified by extraction with boiling benzene, in which it is slightly soluble. It forms soft, white, crystalline flakes, freely soluble in water or alcohol, sparingly so in acetone:

0.1582 gave 0.2564 CO_2 and 0.0810 H_2O . $C=44.20$; $H=5.69$.

0.2061 „ 0.3642 $BaSO_4$. $S=24.27$.

0.1668 „ 0.0451 Na_2SO_4 . $Na=8.76$.

$C_{10}H_{15}O_3S_2Na$ requires $C=44.44$; $H=5.56$; $S=23.70$;
 $Na=8.52$ per cent.

The free *camphor- β -thiosulphonic acid* is oily, and fairly soluble in water. It decomposes extremely readily into free sulphur, the more stable *thio-anhydride*, and other products.

Camphoryl methyl- β -disulphoxide, $C_{10}H_{15}O \cdot S_2O_2 \cdot Me$, resulted on heating equivalent amounts of the above sodium salt and methyl iodide in excess of methyl alcohol for two hours under a reflux condenser. After recrystallising from a mixture of light petroleum and benzene, it formed very small, white needles, melting at 66° :

0.1804 gave 0.3320 CO_2 and 0.1116 H_2O . $C=50.20$; $H=6.87$.

$C_{11}H_{18}O_3S_2$ requires $C=50.40$; $H=6.88$ per cent.

Camphoryl n-butyl- β -disulphoxide, $C_{10}H_{15}O \cdot S_2O_2 \cdot C_4H_9$, obtained by a similar method from sodium camphor- β -thiosulphonate and *n*-butyl iodide in *n*-butyl alcohol, crystallised in colourless, wax-like prisms, and melted at 55° :

0.1248 gave 0.2517 CO_2 and 0.0936 H_2O . $C=55.12$; $H=8.34$.

$C_{14}H_{24}O_3S_2$ requires $C=55.26$; $H=7.91$ per cent.

The author desires heartily to thank Prof. Ph. A. Guye for much encouragement and advice during the course of the investigation.

XCI.—*The Constituents of the Leaves of Prunus Serotina.*

By FREDERICK BELDING POWER and CHARLES WATSON MOORE.

THE leaves of *Prunus serotina*, Ehrhart, commonly known as the Wild Black Cherry, have hitherto never been subjected to a complete chemical examination, and apparently the only information concerning them is a statement by Procter (*Proc. Amer. Pharm. Assoc.*, 1858, 6, 325) that, when macerated with water and distilled, they yield a volatile oil and hydrocyanic acid. As the constituents of the bark of *Prunus serotina* were recently made the subject of a thorough investigation by the present authors (*Trans.*, 1909, 95, 243), it seemed desirable also to examine the leaves of this tree. It has thus been ascertained that the leaves contain the same cyanogenetic compound as the bark, namely, *l*-mandelonitrile glucoside, although in relatively smaller amount, but, as was anticipated, there are interesting differences with respect to the other constituents. A complete summary of the results of the present investigation is given at the end of this paper.

EXPERIMENTAL.

The material employed in this investigation consisted of the air-dried leaves of *Prunus serotina*, Ehrhart, which had been very kindly supplied to us by Professor J. U. Lloyd, of Cincinnati, Ohio, to whom our thanks are due. The leaves were gathered under the personal supervision of Professor Lloyd during the month of August, at a time when they were fully matured, and when the fruit of the tree was ripe.

In order to determine the amount of hydrogen cyanide yielded by the leaves, a portion (25 grams) of the finely-crushed material was macerated with water in a tightly closed flask for several days at a temperature of 20—25°. Steam was then passed through the mixture, and the distillate collected in a very dilute solution of sodium hydroxide. After the addition of a little sodium chloride, the product of distillation was titrated with a decinormal solution of silver nitrate. The amount of the latter solution required for 25 grams of material was 0.4 c.c., being thus equivalent to 0.0086 per cent. of HCN.

A portion of the leaves was tested for the presence of an alkaloid, but with a negative result.

Twenty grams of the crushed leaves were successively extracted

in a Soxhlet apparatus with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0.74	gram	= 3.70	per cent.
Ether	0.83	"	= 4.15	"
Chloroform	0.20	"	= 1.00	"
Ethyl acetate	0.34	"	= 1.70	"
Alcohol	3.10	"	= 15.50	"

Total 5.21 grams = 26.05 per cent.

For the purpose of a complete examination, a quantity (12.59 kilograms) of the crushed leaves was extracted by continuous percolation with hot alcohol. After the removal of the greater portion of the alcohol, a viscid, dark green extract was obtained, amounting to 6.66 kilograms.

Distillation of the Extract with Steam: Separation of an Essential Oil.

A quantity (2 kilograms) of the above-mentioned extract, representing 3.78 kilograms of leaves, was mixed with water, and steam passed through the mixture for several hours. The aqueous distillate, which amounted to about 5 litres, contained some drops of oil floating on the surface. It was extracted with ether, the ethereal liquid being washed, dried, and the solvent removed, when 0.2 gram of an aromatic essential oil was obtained. The amount of this oil was not sufficient for its examination.

Non-volatile Constituents of the Extract.

After the distillation of the extract in a current of steam, as above described, there remained in the distillation flask a quantity of a green resin (A) and a dark-coloured, aqueous liquid. The latter was separated by filtration while still hot, and the resin repeatedly treated with boiling water until nothing further was removed. The aqueous liquid and the washings from the resin were united, and may be designated as (B).

Examination of the Green Resin (A).

This resin, at the ordinary temperature, was a dark green, waxy solid, and amounted to 206 grams. It was dissolved in alcohol and mixed with purified sawdust, the thoroughly dried mixture being then successively extracted in a Soxhlet apparatus with petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract formed a dark green, waxy solid, and amounted to 99 grams.

Isolation of Pentatriacontane, $C_{35}H_{72}$, and Hentriacontane, $C_{31}H_{64}$.

The entire amount of the petroleum extract was dissolved in a large volume of warm ether, and the solution kept for several hours, when a small quantity of an almost colourless substance separated. This was collected and washed with cold ether, after which it was distilled under a pressure of 15 mm. The distillate, which rapidly solidified, was crystallised from ethyl acetate, when 0.3 gram of a substance was obtained in small, colourless, glistening leaflets, melting at 74—75°. (Found, C=84.9; H=14.7. Calc., C=85.4; H=14.6 per cent.)

This substance therefore was pentatriacontane.

The ethereal liquid from which the pentatriacontane had been removed, as above described, was successively shaken with aqueous solutions of sodium carbonate and sodium hydroxide, which, however, removed nothing. The ether was accordingly evaporated, and the residue hydrolysed by boiling with an alcoholic solution of potassium hydroxide, after which the alcohol was removed, water added, and the alkaline solution of potassium salts extracted with ether. The ethereal liquid was washed, dried, and then concentrated to a volume of about 150 c.c., when, on cooling, a quantity of a crystalline substance separated. This was collected, washed with a little cold ether, and then recrystallised from a large volume of ethyl acetate, when it was obtained in the form of colourless, glistening leaflets, which melted at 68—69°. The amount of substance so obtained was 5 grams. (Found, C=85.3; H=15.1. Calc., C=85.3; H=14.7 per cent.)

The substance was thus identified as hentriacontane.

Isolation of Ceryl Alcohol, $C_{27}H_{56}O$.

The ethereal filtrate from the hentriacontane was evaporated to remove all the solvent, when a quantity of brown, resinous material was obtained, which appeared to consist of a mixture of hydrocarbons and an alcohol of high carbon content. The mixture was accordingly heated for some hours, at 150°, with an equal weight of phthalic anhydride, in order to convert any alcohol present into its acid phthalic ester, and thus effect its separation. The product of this operation was subsequently digested with a mixture of ether and chloroform, the solution filtered, and shaken with aqueous

sodium carbonate, when an insoluble compound was deposited, which was evidently the sodium salt of an acid phthalic ester. This was collected, washed with a little ether and water, and then hydrolysed by boiling for some time with an alcoholic solution of potassium hydroxide. On cooling, a quantity of a colourless substance separated, which was collected, washed with a little alcohol, and crystallised from a large volume of alcohol, when it was obtained in colourless, glistening plates, melting at 79° . (Found, $C=81.5$; $H=14.1$. Calc., $C=81.8$; $H=14.1$ per cent.)

This substance was thus identified as ceryl alcohol.

The ether-chloroform solution from which the ceryl alcohol had been removed, as above described, was evaporated, and the residue heated with alcoholic potassium hydroxide in order to hydrolyse unchanged phthalic anhydride. The alcohol was then evaporated, water added, and the insoluble portion extracted with ether, the ethereal liquid being washed, dried, and the solvent removed. A quantity of a waxy solid was thus obtained, which distilled between 170° and $300^{\circ}/15$ mm., but from which no pure substance could be isolated. It appeared to consist of a mixture of hydrocarbons.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The aqueous, alkaline solution of potassium salts, from which the hentriacontane and ceryl alcohol had been removed by extraction with ether, was acidified, and again extracted with ether. The ethereal liquid was washed, dried, and concentrated to a volume of about 500 c.c., when, on keeping for several hours, a small quantity of a dark green powder separated. This was collected, washed with ether, and crystallised from dilute pyridine, when it was obtained in colourless, microscopic needles, melting at 295° . This substance possessed the characteristic properties of ipuranol (Trans., 1909, **95**, 249), with which it evidently was identical. It yielded an acetyl derivative, which separated in glistening leaflets, melting at 163° , and when this was mixed with a little diacetyl-ipuranol the melting point remained unchanged. The amount of substance obtained was too small for analysis.

Examination of the Fatty Acids.

The ethereal filtrate from the ipuranol was concentrated somewhat, and then mixed with a large volume of light petroleum, when a quantity of chlorophyll was precipitated. This was removed by filtration, and the filtrate evaporated, when a quantity (12 grams) of fatty acids was obtained, which, when distilled under diminished pressure, passed over between 225° and $237^{\circ}/12$ mm.

Nine grams of the mixed acids were converted into their lead salts, and the latter digested with ether, when the greater portion dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the regenerated fatty acids purified by distillation under diminished pressure. The soluble portion of the lead salts yielded 6 grams of liquid acids, whilst the insoluble portion gave 2.5 grams of solid acids.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over at about $230^{\circ}/12$ mm. An analysis and a determination of the iodine value gave the following results:

0.1232 gave 0.3490 CO_2 and 0.1255 H_2O . $\text{C}=77.2$; $\text{H}=11.3$.

0.2190 absorbed 0.4337 iodine. Iodine value=198.0.

$\text{C}_{18}\text{H}_{32}\text{O}_2$ requires $\text{C}=77.1$; $\text{H}=11.4$ per cent. Iodine value=181.4.

$\text{C}_{18}\text{H}_{30}\text{O}_2$ „ $\text{C}=77.7$; $\text{H}=10.8$ „ Iodine value=274.0.

In order to obtain more definite information respecting the nature of the above mixture, a quantity of it was oxidised according to the method described by Lewkowitsch (*Chemical Technology and Analysis of Oils, Fats, and Waxes*, 1904, vol. I, p. 360). This resulted in the formation of tetrahydroxystearic acid (m. p. 157 — 160°) and a very small quantity of a hexahydroxystearic acid, melting at 170 — 172° . It may thus be concluded that the liquid acids consisted chiefly of a mixture of linolic and isolinolenic acids, the former in predominating amount.

The Solid Acids.—These acids melted at 53 — 55° , and on analysis gave the following result:

0.1564 gave 0.4305 CO_2 and 0.1750 H_2O . $\text{C}=75.1$; $\text{H}=12.4$.

$\text{C}_{16}\text{H}_{32}\text{O}_2$ requires $\text{C}=75.0$; $\text{H}=12.5$ per cent.

$\text{C}_{18}\text{H}_{36}\text{O}_2$ „ $\text{C}=76.1$; $\text{H}=12.7$ „

From this result it would appear that the solid acids consisted of a mixture of palmitic and stearic acids, the former predominating.

Ethereal Extract of the Resin.

This extract, after the complete removal of the solvent, amounted to 70 grams. As originally obtained, it consisted of a dark green, ethereal liquid, containing a quantity of an amorphous, green, sparingly soluble powder. The latter was collected on a filter, and washed well with ether, when it amounted to about 35 grams. On concentrating the ethereal filtrate to about 500 c.c., a further quantity (7 grams) of a similar amorphous powder was obtained.

Isolation of a New Crystalline Substance, Prunol,
 $C_{31}H_{48}O(OH)_2 \cdot H_2O$.

The above-mentioned portions of solid material were separately examined, but proved to be identical. Its purification was found to be best accomplished by the following method: 30 grams of the material were mixed with 300 c.c. of cold alcohol, and subsequently about 300 c.c. of dilute sodium carbonate solution added. The liquid was filtered to remove a considerable quantity of a dark green resin, and the pale green filtrate boiled for a short time with animal charcoal, filtered while still hot, and concentrated on a water-bath until nearly all the alcohol had been expelled, when a substance separated in long, colourless needles. This was collected, washed with a little cold water, and recrystallised from a solution of sodium carbonate in dilute alcohol, in the manner described above. The product thus obtained, consisting of a sodium derivative, was readily soluble in strong or dilute alcohol, but almost insoluble in water. When boiled with water, it appeared to undergo partial dissociation. On adding hydrochloric acid to a solution of the sodium derivative in dilute alcohol, the parent substance is liberated. The latter separates from dilute alcohol in colourless, hair-like crystals, melting at 275—277°:

0.3262, on heating at 125°, lost 0.0126 H_2O . $H_2O = 3.8$.

0.1502 * gave 0.4335 CO_2 and 0.1474 H_2O . $C = 78.7$; $H = 10.9$.

$C_{31}H_{50}O_3 \cdot H_2O$ requires $H_2O = 3.7$ per cent.

$C_{31}H_{50}O_3$ requires $C = 79.1$; $H = 10.6$ per cent.

The sodium derivative gave on analysis the following results:

0.4474, on heating at 125°, lost 0.0299 H_2O . $H_2O = 6.7$.

0.3136 * gave, on ignition, 0.0330 Na_2CO_3 . $Na = 4.6$.

$C_{31}H_{49}O_3Na \cdot 2H_2O$ requires $H_2O = 6.8$ per cent.

$C_{31}H_{49}O_3Na$ requires $Na = 4.7$ per cent.

These results render it evident that the above-described substance possesses the formula $C_{31}H_{50}O_3$. The only other known substance of this formula is that obtained by Power and Tutin from olive leaves, which was designated oleanol (Trans., 1908, **93**, 896). Although these two substances are very similar in their chemical properties, and are evidently closely related, they are not identical. The substance obtained from the leaves of *Prunus serotina* being therefore a new compound, it is proposed to designate it *prunol*, with reference to the generic name of the plant.

Prunol, $C_{31}H_{48}O(OH)_2 \cdot H_2O$, is sparingly soluble in ether, chloroform, ethyl acetate, and cold alcohol, but dissolves readily in hot

* Anhydrous substance.

alcohol. If to its solution in acetic anhydride a few drops of concentrated sulphuric acid are added, a fine pink colour is produced, which slowly passes through violet to blue, finally becoming green.

Two of the oxygen atoms contained in prunol are, as shown below, present in the form of hydroxyl groups, one of which possesses phenolic properties, whilst the other is evidently alcoholic, as only a mono-sodium derivative could be obtained. The state of combination of the third oxygen atom is not known, but it was ascertained by means of Perkin's modification of the Zeisel method that no methoxyl or ethoxyl group was present.

Diacetylprunol, $C_{31}H_{48}O_3(CO \cdot CH_3)_2$.—This was obtained by heating prunol with acetic anhydride. The resulting liquid, when concentrated and kept for some time, slowly deposited the *diacetyl* derivative in handsome, glistening needles, which melted at 181° :

0.1442 gave 0.3995 CO_2 and 0.1255 H_2O . $C=75.6$; $H=9.7$.

$C_{35}H_{54}O_5$ requires $C=75.8$; $H=9.7$ per cent.

A determination of its specific rotatory power gave the following result:

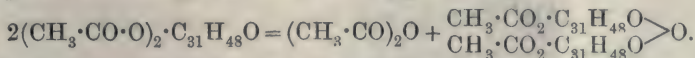
0.1814, made up to 20 c.c. with chloroform, gave $\alpha_D +1.08'$ in a 2-dcm. tube, whence $[\alpha]_D +62.4^\circ$.

Diacetylprunol is readily soluble in ether, chloroform, and ethyl acetate, and also in hot alcohol, but is only moderately soluble in cold alcohol. As already stated, it melts at 181° , but if the temperature is raised to about 220° , acetic anhydride is evolved and the mass solidifies, after which it only melts above 300° . The substance so obtained is insoluble in boiling alcohol, but dissolves readily in benzene. If to its solution in boiling benzene hot alcohol is added, the substance is obtained in small, glistening, colourless plates, which melt at about 315° :

0.1546 gave 0.4434 CO_2 and 0.1404 H_2O . $C=78.2$; $H=10.1$.

$C_{66}H_{102}O_7$ requires $C=78.7$; $H=10.1$ per cent.

This result indicates that on heating diacetylprunol two molecules of the compound lose one molecule of acetic anhydride, the residual complexes becoming united by an oxygen atom, as follows:



A somewhat similar change takes place on heating diacetyl-oleanol (*loc. cit.*, p. 898), but in this case both the acetyl groups are eliminated from one molecule of the compound.

Monoacetylprunol, $C_{31}H_{48}O_2(OH) \cdot CO \cdot CH_3$.—If diacetylprunol is dissolved in hot 70 per cent. alcohol, and the solution boiled for about two hours, one acetyl group is removed, and, on cooling the

solution, the *monoacetyl* derivative separates in small, colourless needles, which melt at 290° :

0.1202 gave 0.3394 CO_2 and 0.1120 H_2O . $\text{C}=77.0$; $\text{H}=10.4$.

$\text{C}_{33}\text{H}_{52}\text{O}_4$ requires $\text{C}=77.3$; $\text{H}=10.2$ per cent.

This monoacetyl derivative is neutral towards sodium hydroxide, and it may therefore be concluded that the hydroxyl group regenerated by the above-described change is not the one which possesses a phenolic character.

Monomethylprunol, $\text{C}_{31}\text{H}_{48}\text{O}(\text{OH})\cdot\text{O}\cdot\text{CH}_3$.—Two grams of prunol were dissolved in absolute alcohol, and an excess of both sodium ethoxide and methyl iodide added. The mixture was then boiled for about an hour, after which the greater portion of the solvent was removed. On the subsequent addition of water, the *mono-methyl* derivative slowly separated in long, hair-like crystals. It was recrystallised from dilute alcohol, when it melted indefinitely between 110° and 115° . If dried at 100° , and then crystallised from absolute alcohol, it melted at 164 — 165° . After drying in a desiccator, it gave on analysis the following results:

0.1440 gave 0.4044 CO_2 and 0.1380 H_2O . $\text{C}=76.6$; $\text{H}=10.6$.

0.2580 gave, by Perkin's modification of Zeisel's method, 0.1190

AgI . $\text{OMe}=6.1$.

0.4405, on prolonged heating at 100° , lost 0.0167 H_2O . $\text{H}_2\text{O}=3.8$.

$\text{C}_{32}\text{H}_{52}\text{O}_3\cdot\text{H}_2\text{O}$ requires $\text{C}=76.5$; $\text{H}=10.7$; $\text{OMe}=6.1$;

$\text{H}_2\text{O}=3.6$ per cent.

Acetylmethylprunol, $\text{C}_{31}\text{H}_{48}\text{O}_2(\text{O}\cdot\text{CH}_3)\cdot\text{CO}\cdot\text{CH}_3$.—Monomethylprunol was dissolved in acetic anhydride, and the solution boiled for an hour. The liquid was then somewhat concentrated, and allowed to cool, when *acetylmethylprunol* separated in glistening leaflets, which melted at 235° :

0.1512 gave 0.4290 CO_2 and 0.1390 H_2O . $\text{C}=77.4$; $\text{H}=10.2$.

$\text{C}_{34}\text{H}_{54}\text{O}_4$ requires $\text{C}=77.6$; $\text{H}=10.3$ per cent.

The original ethereal liquid from which the crude prunol had been separated was thoroughly examined, but, apart from a further small quantity of prunol, nothing definite could be isolated from it.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

These extracts amounted to 7, 5, and 15 grams respectively, and consisted entirely of resinous material.

Examination of the Aqueous Liquid (B).

This liquid, as already indicated, represented that portion of the original alcoholic extract of the leaves which was soluble in hot

water, and from which the previously-described resin (A) had been removed.

Isolation of Benzoic Acid.

The aqueous liquid, which, on being kept for some time, had deposited a quantity of a brown, amorphous powder, was thoroughly extracted with ether, the combined ethereal liquids being washed, dried, and the solvent removed. A quantity of an amorphous product was thus obtained, which was subjected to prolonged distillation with steam. The distillate had an acid reaction, and, on extraction with ether, yielded about 1 gram of a crystalline substance, melting at 120° . (Found, $C=68.7$; $H=5.0$. Calc., $C=68.8$; $H=4.9$ per cent.) This substance thus proved to be benzoic acid.

Isolation of Quercetin.

After completely removing the benzoic acid from the ether extract by distillation with steam, as above described, the solid material remaining in the distillation flask was repeatedly extracted with boiling water. On cooling the aqueous liquid, a small quantity (0.7 gram) of a light yellow, amorphous powder was precipitated. This was collected, washed with a little ether, and crystallised from dilute alcohol, when it separated in small, yellow needles, melting at $310-312^{\circ}$.

This substance showed all the properties of quercetin; it was soluble in alkalis, gave crystalline salts with sulphuric and hydrochloric acids, and responded to the colour test with ferric chloride. Its identity with quercetin was confirmed by an analysis (Found, $C=59.8$; $H=3.5$. Calc., $C=59.6$; $H=3.3$ per cent.), and the preparation of its penta-acetyl derivative, which formed small, colourless needles, melting at 194° , and when mixed with a little penta-acetylquercetin the melting point remained unchanged.

As already noted, the aqueous liquid (B), on being kept for some time, deposited a quantity of a brown, amorphous powder. This was not removed before the above-described extraction with ether, and by this treatment it became dissolved in the aqueous liquid. On subsequently removing the ether contained in the aqueous liquid by means of a current of air, the brown powder was again precipitated. It was collected, and amounted to 35 grams, but, although thoroughly examined, nothing definite could be isolated from it.

Isolation of a New Glucoside, Serotrin, $C_{21}H_{20}O_{12} \cdot 3H_2O$.

The aqueous liquid, from which the benzoic acid and quercetin had been removed by extraction with ether, and from which the

above-described brown powder had been separated by filtration, was thoroughly extracted with successive portions of amyl alcohol. These extracts were united, washed with water, and concentrated under diminished pressure to a syrupy consistency. The dark-coloured residue thus obtained was dissolved in a small quantity of hot ethyl alcohol, and the solution kept for some time, when a substance was deposited in light yellow needles. This was collected, washed with a little alcohol, and recrystallised, first from alcohol, and then from dilute pyridine, when it separated in golden-yellow leaflets, melting at 245° . The amount of substance so obtained was 4 grams:

0.3270 of air-dried substance, when heated at 125° , lost 0.0347 H_2O . $\text{H}_2\text{O} = 10.6$.

0.1505 * gave 0.2994 CO_2 and 0.0620 H_2O . $\text{C} = 54.3$; $\text{H} = 4.5$.

$\text{C}_{21}\text{H}_{20}\text{O}_{12}$ requires $\text{C} = 54.3$; $\text{H} = 4.3$ per cent.

$\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot 3\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 10.4$ per cent.

The anhydrous substance, on exposure to the air, readily takes up its three molecules of water of crystallisation:

0.5340 of anhydrous substance absorbed 0.0640 H_2O . $\text{H}_2\text{O} = 12.0$.

$\text{C}_{21}\text{H}_{20}\text{O}_{12}$, to form $\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot 3\text{H}_2\text{O}$, requires $\text{H}_2\text{O} = 11.6$ per cent.

The glucosidic character of the substance was ascertained by boiling it for a few minutes with 5 per cent. aqueous sulphuric acid. The products thus obtained were quercetin, $\text{C}_{15}\text{H}_{10}\text{O}_7$, and a sugar, the latter yielding *d*-phenylglucosazone, melting at $205-208^{\circ}$:

0.7410 of anhydrous substance gave, on hydrolysis, 0.4785 of quercetin. $\text{C}_{15}\text{H}_{10}\text{O}_7 = 64.6$.

$\text{C}_{21}\text{H}_{20}\text{O}_{12}$ requires $\text{C}_{15}\text{H}_{10}\text{O}_7 = 65.1$ per cent.

The quercetin thus obtained was identified by its analysis (Found, $\text{C} = 59.6$; $\text{H} = 3.7$. Calc., $\text{C} = 59.6$; $\text{H} = 3.3$ per cent.), and also by that of its acetyl derivative (Found, $\text{C} = 58.6$; $\text{H} = 4.1$. Calc., $\text{C} = 58.6$; $\text{H} = 3.9$ per cent.).

From these results it is evident that the above-described substance is a glucoside of quercetin. It was thought that it might be identical with a glucoside recently isolated by A. G. Perkin (Trans., 1909, 95, 2181) from cotton flowers, and designated quercimeritrin, since the latter possesses the formula $\text{C}_{21}\text{H}_{20}\text{O}_{12} \cdot 3\text{H}_2\text{O}$, melts at $247-249^{\circ}$, and yields quercetin on hydrolysis. Through the courtesy of Professor A. G. Perkin, who had kindly supplied us with a specimen of quercimeritrin, it was possible to compare the two substances, and they were found not to be identical. The above-described glucoside is more readily soluble in water, and also more readily hydrolysed, than quercimeritrin. Furthermore, on

* Dried at 125° .

mixing the two substances, the melting point of the mixture was found to be considerably lower than that of either of the constituents. Inasmuch as the glucoside obtained from the leaves of *Prunus serotina* does not agree in its properties with any of the previously-described glucosides of quercetin, it must be regarded as a new compound. It is therefore proposed to designate it *serotrin*, with reference to the specific name of the plant.

Serotrin, $C_{21}H_{20}O_{12} \cdot 3H_2O$, is sparingly soluble in cold, and fairly readily soluble in boiling water or alcohol. It dissolves in alkalis with a dark yellow colour, and in aqueous solution it gives with lead acetate an orange-red precipitate.

Octa-acetylserotrin, $C_{21}H_{12}O_{12}(CO \cdot CH_3)_8$.—Two grams of serotrin were boiled for two hours with 25 grams of acetic anhydride. The solution so obtained was poured into water, and, after some time, the whole was extracted with ether. The ethereal liquid was washed with dilute aqueous sodium hydroxide, and then with water, after which it was dried and the solvent removed. The residue so obtained was crystallised, first from a mixture of alcohol and acetic acid, and finally from ether, when *octa-acetylserotrin* separated in colourless needles, melting at 150° :

0.1434 gave 0.2910 CO_2 and 0.0630 H_2O . $C = 55.3$; $H = 4.8$.

$C_{21}H_{12}O_{12}(CO \cdot CH_3)_8$ requires $C = 55.5$; $H = 4.5$ per cent.

Octa-acetylserotrin is sparingly soluble in ether or cold alcohol, but readily soluble in acetic acid. A determination of its specific rotatory power gave the following result:

0.2005, made up to 20 c.c. with chloroform, gave $\alpha_D - 1^\circ 32'$ in a 2-dcm. tube, whence $[\alpha]_D - 76.4^\circ$.

The glucoside serotrin appears to be accompanied in the leaves of *Prunus serotina* by a closely related substance containing a methoxyl group, but the amount of this constituent was too small to permit of its isolation.

Identification of l-Mandelonitrile Glucoside.

The original alcoholic filtrate from the crude serotrin was mixed with water and subjected to a vigorous distillation in a current of steam until all the amyl and ethyl alcohols had been removed. The aqueous liquid so obtained was cooled, filtered, and treated with a solution of basic lead acetate. This produced a voluminous yellow precipitate, which was removed by filtration and carefully examined, but nothing definite could be isolated from it.

The filtrate from the basic lead acetate precipitate, after the addition of a little sodium acetate, was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to dryness. A small

quantity of the residue thus obtained was dissolved in water and treated with emulsin, when hydrogen cyanide and benzaldehyde were produced. The residue was accordingly extracted with absolute alcohol, and the alcoholic solution concentrated to the volume of 200 c.c. On cooling, a small quantity of resinous material separated, which was removed, and to the clear liquid an equal volume of dry ethyl acetate was added, when a further precipitation occurred. The clear liquid was separated by decantation, concentrated to the volume of 50 c.c., and dissolved in 200 c.c. of ethyl acetate. On the addition of an equal volume of dry ether, a further quantity of resinous material was deposited. After some hours the clear liquid was evaporated to dryness, and the residue extracted with small quantities of dry ethyl acetate, when, after the removal of the solvent, an uncrystallisable syrup was obtained. This was subsequently boiled for a few minutes with twenty times its weight of acetic anhydride, in the presence of a little camphorsulphonic acid, with the view of converting the glucoside into a more readily crystallisable acetyl derivative. The mixture so obtained was poured into water, and after some hours was extracted with ether, the ethereal liquid being subsequently shaken with a 5 per cent. solution of sodium hydroxide, in order to remove small amounts of acidic substances, and afterwards washed with water. On concentrating the ethereal liquid to a small bulk, and inoculating it with a trace of tetra-acetyl-*l*-mandelonitrile glucoside, the acetyl derivative at once separated in long needles. It was crystallised from alcohol, when it melted at 136° , and when mixed with a little pure tetra-acetyl-*l*-mandelonitrile glucoside the melting point remained unchanged. The amount of this acetyl derivative obtained from 2 kilograms of the alcoholic extract, representing 3.78 kilograms of the leaves, was only about 0.25 gram (Found, C=57.0; H=5.6. Calc., C=57.0; H=5.6 per cent.).

Although the amount of the cyanogenetic compound present in the leaves was too small to permit of its direct isolation, the characters of the above-described acetyl derivative afford conclusive evidence of its identity as *l*-mandelonitrile glucoside.

The *l*-mandelonitrile glucoside is accompanied in the leaves by an enzyme, which may be obtained by adding to a cold aqueous infusion of them a large volume of alcohol. The precipitate thus produced formed, when dry, a dark brown powder, and amounted to about 0.9 per cent. of the weight of leaves employed. It contains a large proportion of inorganic material, but slowly hydrolyses β -glucosides.

The aqueous liquid, after having been extracted with amyl

alcohol as above described, was subjected to a vigorous distillation in a current of steam, in order to remove any dissolved amyl alcohol. The liquid was then allowed to cool, and treated with a solution of basic lead acetate. This produced a voluminous, orange-yellow precipitate, which was collected, washed, and then suspended in water and decomposed by hydrogen sulphide. On filtering the mixture, a liquid was obtained which evidently contained a quantity of tannin, but nothing definite could be separated from it. The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure to a volume of about 1.5 litres. It contained a considerable quantity of a sugar, since it readily yielded *d*-phenylglucosazone, melting at 210°.

Isolation of l-Mandelic Acid.

To the above-mentioned aqueous liquid 150 grams of sulphuric acid were added, and the mixture boiled for some hours. A quantity of insoluble, red, resinous material was thus formed, which was removed by filtration and examined, but nothing definite could be obtained from it. The aqueous filtrate was thoroughly extracted with ether, the united ethereal liquids being washed with water, dried, and the solvent removed. A quantity (2.5 grams) of a crystalline residue was thus obtained, which, after recrystallisation from benzene, separated in handsome, flat needles, melting at 132° (Found, C=63.3; H=5.2. Calc., C=63.2; H=5.2 per cent.).

A determination of the specific rotatory power of this substance gave the following result:

0.3112, made up to 20 c.c. with water, gave $\alpha_D -4^{\circ}54'$ in a 2-dm. tube, whence $[\alpha]_D -157.4^{\circ}$.

The substance was thus identified as *l*-mandelic acid, and its isolation from the aqueous liquid, after hydrolysis, would indicate that only a small part of the *l*-mandelonitrile glucoside present had been removed by extraction with amyl alcohol, as above described.

Summary.

The results of this investigation may be summarised as follows:

The material employed, consisting of the air-dried leaves of *Prunus serotina*, Ehrhart, yielded, on maceration with water, an amount of hydrogen cyanide equivalent to 0.0086 per cent. of its weight. The leaves contain a relatively small amount of *l*-mandelonitrile glucoside, $C_{14}H_{17}O_6N$, which was identified by means of its tetra-acetyl derivative (m. p. 136°), together with an enzyme which hydrolyses β -glucosides.

An alcoholic extract of the leaves, when distilled in a current of

steam, yielded a very small amount of an essential oil, but no hydrogen cyanide. The non-volatile constituents of the leaves, as obtained after treating the alcoholic extract with steam, consisted of a green resin, which was insoluble in either hot or cold water, and material which remained dissolved in the aqueous liquid. The resin, which amounted to about 5.5 per cent. of the weight of the leaves, yielded hentriacontane, pentatriacontane, ceryl alcohol, palmitic, stearic, linolic, and *isolinolenic* acids, a small amount of ipuranol, $C_{23}H_{38}O_2(OH)_2$, and a new, crystalline substance, $C_{31}H_{48}O(OH)_2$, melting at 275—277°, which has been designated *prunol*.

The portion of the alcoholic extract of the leaves which was soluble in water, and from which the above-described resin had been removed, contained benzoic acid, quercetin, a new glucoside of quercetin, $C_{21}H_{20}O_{12} \cdot 3H_2O$ (m. p. 245°), which has been designated *serotrin*, and *l*-mandelonitrile glucoside, together with a quantity of sugar and tannin. The aqueous liquid, after heating with dilute sulphuric acid, yielded, furthermore, *l*-mandelic acid, which had evidently been formed by the hydrolysis of the *l*-mandelonitrile glucoside.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XCII.—*The Intramolecular Rearrangement of the Halides of Phenazothionium.*

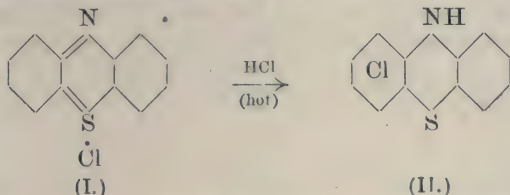
By HAROLD JAMES PAGE and SAMUEL SMILES.

DURING the investigation of the action of acid reagents on the ortho-sulphoxides of diphenylamine, the reduction of the chloride of *N*-methylphenazothionium was undertaken. It was found that the product of reduction consisted for the greater part of *N*-methylthiodiphenylamine, but a small quantity of a chloro-derivative was isolated at the same time. Experiments were then made to ascertain the nature and origin of this halogen derivative, and it was found that the substance was chloro-*N*-methylthiodiphenylamine, and that this was formed by the action of hydrochloric acid, employed in the reducing agent, on the phenazothionium salt.

The investigation was then extended to salts of other phenazothionium derivatives in order to determine whether the reaction is of general application, and whether it could be employed as a

general method of chlorinating the derivatives of thiodiphenylamine.

The reaction essentially consists of the conversion of the azo-thionium salt (I) by the action of hot concentrated acid into the halogen derivative of thiodiphenylamine (II), and, taking the simplest case as an example, it may be formulated as follows:

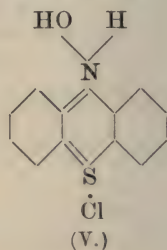
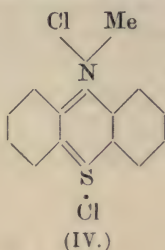
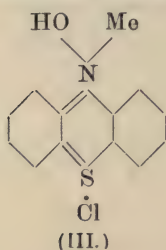


It is worthy of notice that the process is analogous to that which takes place during the interaction of hydrochloric acid and *p*-benzoquinone when chloroquinol is formed, since chlorination and reduction take place simultaneously. The reaction clearly affords additional support to the quinonoid structure usually given to the salts of phenazothionium, particularly to that of the *N*-methylphenazothionium salt, which was discussed in a previous paper (Barnett and Smiles, this vol., p. 186) dealing with the intramolecular rearrangement of *N*-methyldiphenylamine *o*-sulphoxide.

So far as the present experiments have been carried, it seems that the reaction is controlled by the nature of the halogen acid employed, and by the nature and number of the substituents present in the thiodiphenylamine complex. With hydrochloric acid the conversion of phenazothionium chloride into chlorothiodiphenylamine is readily effected, but with hydriodic acid the reaction seems not to take place, whilst with hydrobromic acid the yield of bromothiodiphenylamine is very small. Dinitrophenazothionium, on the other hand, is only very slightly attacked even by hydrochloric acid at a higher temperature, and we have not been able to isolate the product in sufficient quantity for examination; but from experiments which are later described it appears that the dichloro-derivative is readily attacked by this reagent.

From the composition of the initial and final products of this reaction (for example, I and II), it would seem that the process is merely an intramolecular rearrangement, but whether this is actually the case or not is very difficult to decide satisfactorily. All that can at present be said of the mechanism of the reaction is that probably a di-acid salt of phenazothionium is first formed, for the presence of acid seems essential, the action of heat alone being without effect. In the case of the *N*-methyl compound, which is isolated as the mono-acid salt (III), there is no doubt that the

di-acid salt (IV) would be formed in presence of strong acids, and the same may be inferred of the unsubstituted derivatives, which contain an additional molecule of water, and are probably ammonium hydroxides (V) (Barnett and Smiles, this vol., p. 186):



The Chlorination of Thiodiphenylamine.

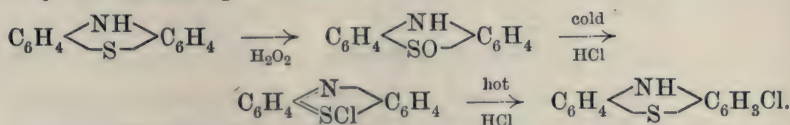
The chlorination of thiodiphenylamine has been previously investigated by Unger and Hoffmann (*Ber.*, 1896, **29**, 1362). These experimenters found that the direct action of chlorine on thiodiphenylamine in chloroform solution is unsatisfactory, much resinous material being formed with only a small quantity of tetrachlorothiodiphenylamine. They observed, however, that if thiodiphenylamine is treated in ethereal solution with nitrous vapours, an insoluble brown compound is formed, and this, on warming with hydrochloric acid in suitable media, gave a mixture of mono-, di-, and tetra-chlorothiodiphenylamine. Unger and Hoffmann were at that time unable to determine the nature of the intermediate product which was obtained from thiodiphenylamine with nitrous vapours; but from the later experiments of Kehrmann (*Ber.*, 1901, **34**, 4170) on the acid oxidation of this sulphide, there can be little doubt that it was a salt of phenazothionium, probably the impure nitrate. It is evident that this view is strongly supported by the discovery of the reaction which is described in the present paper.

Our experiments have shown that if the pure phenazothionium chloride is warmed with excess of hydrochloric acid, the mono- and di-chloro-derivatives of thiodiphenylamine are formed at the same time. In passing, it may be mentioned that we have been able to confirm the observation of Unger and Hoffmann, that these substances are isomorphous and crystallise together in the proportion of $5C_{12}H_8NSCl : 2C_{12}H_7NSCl_2$. The mixture is difficult to resolve by fractional crystallisation, but we have been able to demonstrate the presence of the monochloro-derivative by nitration, which yields the monochlorodinitrodiphenylamine sulphoxide. Unger and Hoffmann did not definitely prove the occurrence of this

monochloro-derivative, but inferred its presence from the chlorine content and absorption spectra of impure specimens.

The action of hydrochloric acid on the chloride of *N*-methylphenazothionium yielded only the monochloro-*N*-methylthiodiphenylamine. The proof that the methyl group has not become detached from the nitrogen during the reaction is given by the properties of the dinitrosulphoxide, which is prepared by the action of nitric acid on the methylchloro-compound. This nitro-compound is quite insoluble in aqueous alkali hydroxide, whilst the corresponding imino-derivative is readily soluble therein, giving orange-coloured solutions of the alkali salt.

In obtaining these chloro-derivatives we have avoided the isolation of the somewhat unstable phenazothionium salts by preparing them in solution from the intramolecular rearrangement of the corresponding diphenylamine *o*-sulphoxides in presence of acids (Barnett and Smiles, *Trans.*, 1909, **95**, 1253; this vol., p. 186); and since these sulphoxides (*loc. cit.*) are formed by the neutral oxidation of thiodiphenylamine, the whole process of chlorination may be summed up as follows:



It will be observed that each of the two intermediate products in this process may be isolated and separately treated in the manner indicated; but experiment has shown that this is unnecessary, and if hydrogen dioxide is mixed with an alcoholic solution of thiodiphenylamine acidified with hydrochloric acid, chlorination proceeds energetically. In preparing the mono- or di-chloro-compounds, the direct process is not to be recommended, for, even if the calculated amount of hydrogen dioxide is taken, mixtures of various chloro-derivatives are formed. The process is seen to its best advantage in preparing the tetrachlorothiodiphenylamine, which is obtained in excellent yield by taking a slight excess of the oxidising agent. In the preparation it would seem that the reactions involved in the above scheme are repeated four times over, but no attempt has been made to isolate the several intermediate products.

EXPERIMENTAL.

Mono- and Di-chlorothiodiphenylamine.

Diphenylamine *o*-sulphoxide was shaken with concentrated aqueous hydrochloric acid, and the deeply coloured solution of phenazothionium chloride which was thus obtained was boiled for

half an hour under reflux. During this treatment the mixture had deposited a crystalline solid, the liquid becoming pale coloured. The whole was repeatedly extracted with ether, which removed the required chloro-derivatives, leaving a small quantity of insoluble by-product. The united ethereal extracts were freed from halogen acid by means of alkali, and then were evaporated. The residue—a mass of green crystals—was recrystallised three or four times from benzene, when colourless plates, which melted at 205–206°, were obtained. Analysis showed that the substance was the isomorphous mixture of mono- and di-chlorothiodiphenylamine previously described by Unger and Hoffmann (*Ber.*, 1896, **29**, 1362):

0.1807 gave 0.3857 CO₂ and 0.0489 H₂O. C=58.3; H=3.0.

0.1925 „ 0.1419 AgCl. Cl=18.22.

5C₁₂H₈NCIS + 2C₁₂H₇NCl₂S requires C=59.0; H=3.1;
Cl=18.2 per cent.

The yield of this substance was about 70 per cent. of the weight of the original sulphoxide. It is readily oxidised in presence of acids, particularly by concentrated sulphuric acid, which dissolves it, giving a cherry-red solution and liberating sulphurous acid.

Monochlorodinitrodiphenylamine Sulphoxide.

The mixture of mono- and di-chlorothiodiphenylamine, which is described in the foregoing paragraph, was gradually added to a mixture of equal quantities of fuming nitric and glacial acetic acids, the liquid being cooled and well shaken after each addition. As soon as all the chloro-compound had dissolved, the solution was poured into a large bulk of cold water, and the precipitated nitro-derivative was collected. After purification by means of acetone, the substance was obtained in minute, yellow needles, which melted at 244°:

0.1670 gave 0.2607 CO₂ and 0.0296 H₂O. C=42.57; H=1.98.

0.2164 „ 0.0945 AgCl. Cl=10.8.

C₁₂H₆O₅N₂ClS requires C=42.41; H=1.77; Cl=10.5 per cent.

Monochlorodinitrodiphenylamine sulphoxide readily dissolves in aqueous alkali hydroxide, giving red solutions of the alkali salt; it is also attacked by an alcoholic solution of hydrogen chloride, furnishing the red phenazothionium derivative. The latter reaction shows the presence of the sulphoxide grouping.

Chloromethylthiodiphenylamine.

N-Methyldiphenylamine sulphoxide was converted by concentrated hydrochloric acid into the phenazothionium chloride, and this was heated with excess of the acid for about half an hour.

The mixture was finally treated in the same manner as previously described with the parent compound. The resulting crystalline mass consisted of the monochloro-derivative in an almost pure condition, and, unlike the behaviour of the preceding derivative of thiodiphenylamine, no dichloro-compound could be found. The substance was recrystallised from lukewarm methyl alcohol, which deposited pure chloro-*N*-methylthiodiphenylamine in large prisms, which melted at 107° :

0.1192 gave 0.2761 CO_2 and 0.0473 H_2O . $\text{C}=63.17$; $\text{H}=4.4$.

0.1886 „ 0.1096 AgCl . $\text{Cl}=14.4$.

$\text{C}_{13}\text{H}_{10}\text{NClS}$ requires $\text{C}=63.03$; $\text{H}=4.04$; $\text{Cl}=14.3$ per cent.

Chloro-N-methylthiodiphenylamine is soluble in concentrated sulphuric acid, being then oxidised and converted into the rose-red derivative of phenazothionium. The reaction which is described in the foregoing paragraph may also be effected by allowing the solid phenazothionium salt, which has been moistened with hydrochloric acid, to remain some days at the atmospheric temperature.

Monochlorodinitro-N-methyldiphenylamine o-Sulphoxide.

The nitration of the chloro-derivative was carried out in the same way as described with chlorothiodiphenylamine. The product was purified by recrystallisation from dilute methyl alcohol, when the pure substance was obtained in bright yellow needles, which melted at 215° :

0.1606 gave 0.2576 CO_2 and 0.0402 H_2O . $\text{C}=43.8$; $\text{H}=2.7$.

0.2121 „ 0.0832 AgCl . $\text{Cl}=9.7$.

$\text{C}_{13}\text{H}_8\text{O}_5\text{N}_3\text{ClS}$ requires $\text{C}=44.1$; $\text{H}=2.3$; $\text{Cl}=10.0$ per cent.

The substance is insoluble in hot aqueous alkali hydroxide, and is converted into the phenazothionium derivative on being set aside a few hours with alcoholic hydrogen chloride. The behaviour with the former reagent shows the absence of the imino-group, whilst that with the latter indicates the presence of the thionyl arrangement.

Bromo-derivatives of Thiodiphenylamine.

Diphenylamine *o*-sulphoxide was treated in a manner similar to that described in the preparation of the chloro-derivatives, only instead of hydrochloric acid, fuming hydrobromic acid was employed. The greater portion of the phenazothionium salt was converted into a brown, crystalline compound, which, being insoluble in ether, remained suspended in the liquid after extraction. This substance was not further examined, but on evaporating the ether a small quantity of a mixture of bromo-derivatives of thiodiphenyl-

amine was obtained. Apparently these are as difficult to separate by fractional crystallisation as the chloro-compounds, for, after repeating the process, a sample was obtained which gave the following numbers on analysis:

0.1394 gave 0.2558 CO_2 and 0.0347 H_2O . $\text{C}=50.7$; $\text{H}=2.7$.

0.1710 „ 0.1190 AgBr . $\text{Br}=29.6$.

$\text{C}_{12}\text{H}_8\text{NBrS}$ requires $\text{C}=51.8$; $\text{H}=2.8$; $\text{Br}=28.7$ per cent.

The quantity of material obtained was not sufficient to permit a complete separation, the yield being extremely small.

In solubility and general chemical behaviour this mixture closely resembles the corresponding chloro-derivatives.

Tetrachlorothiodiphenylamine.

A concentrated solution of thiodiphenylamine in ethyl alcohol was saturated at 0° with hydrochloric acid. A 30 per cent. solution of hydrogen dioxide was then gradually added to the mixture, the molecular proportions of hydrogen dioxide and thiodiphenylamine being as four to one. The reaction proceeded vigorously with evolution of heat, and on setting aside the mixture for about an hour a copious precipitate of the required chloro-derivative separated. This was collected and recrystallised from hot benzene, when it was obtained as a mass of interlaced needles. It melted at $232\text{--}233^\circ$, and gave a deep red solution in hot concentrated sulphuric acid, sulphurous acid being evolved:

0.1955 gave 0.3350 AgCl . $\text{Cl}=42.4$.

$\text{C}_{12}\text{H}_5\text{NCl}_4\text{S}$ requires $\text{Cl}=42.24$ per cent.

The yield obtained by this process is good; for example, 12 grams of thiodiphenylamine furnished 19 grams of the tetrachloro-derivative, or about 75 per cent. of the theoretical.

The oxidation products of this tetrachlorothiodiphenylamine are now being investigated.

In conclusion the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant which has defrayed the expenses of this research.

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XCIII.—*The Salts of 8-Hydroxyquinoline.*

By JOHN JACOB FOX.

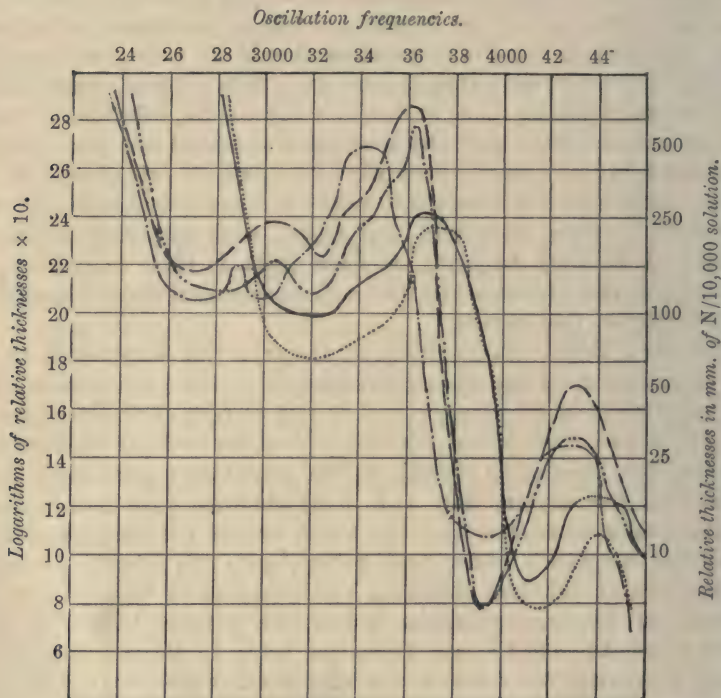
DURING the course of an investigation on certain hydroxyazo-compounds derived from quinoline, the peculiar properties of the derivatives of 8-hydroxyquinoline as compared with the corresponding derivatives of 5- and 8-aminoquinolines rendered it desirable that the salts of 8-hydroxyquinoline should be examined spectroscopically and also as to their hydrolysis. When 8-hydroxyquinoline is dissolved in strong acids or in alkali hydroxides, solutions of deep yellow colour result, and the solid salts obtained are also yellow, whereas 8-hydroxyquinoline in the pure state is colourless. Most of the salts with the commoner metals are buff-coloured or yellow, the salts of copper, cadmium, and nickel being somewhat green in shade. A striking property of these salts is their solubility in chloroform and benzene, the lead and copper salts being especially noteworthy in this respect.

The cause of the yellow colour in the salts was ascertained from an examination of the absorption spectra of the sodium salts and hydrochlorides of 8-hydroxyquinoline and certain of its derivatives. It was found that whilst 8-hydroxyquinoline and its derivatives showed two absorption bands in the ultra-violet portion of the spectrum, the sodium salt and hydrochloride gave two similar bands, but in the latter case the bands nearer the red end of the spectrum are much wider and extend into the visible portion, giving rise to coloured solutions. The feature of the absorption spectra of 8-hydroxyquinoline is the two marked bands in the ultra-violet, the effect of salt formation being to displace the bands towards the red. The colour of the salts is not, therefore, due to any alteration in the structure of the molecule; and this was further established by the examination of hydroxytetrahydroquinoline, in which a profound alteration of structure has obviously been brought about. It will be seen from the curves (pp. 1120 and 1121) that hydroxytetrahydroquinoline gives one strong band in the ultra-violet which is much narrower than in 8-hydroxyquinoline, and the second band has almost disappeared. As regards the hydrochloride of hydroxytetrahydroquinoline, the band has been displaced in the direction of the ultra-violet, and the salt, like the base, is therefore colourless.

From the point of view of the use of 8-hydroxyquinoline in the preparation of hydroxyazo-derivatives, it was necessary to obtain some information as to the degree of hydrolysis of the salts of the

substance acting as a phenol, since the presence of the basic nitrogen in the ortho-position with respect to the hydroxyl group would certainly exert some influence on the hydrolysis of the salts. It was found that 8-hydroxyquinoline hydrochloride was hydrolysed to the extent of 4.2 per cent. at 18° in 0.01*N*-solution, and that of the sodium salt of hydroxyquinoline, 11.6 per cent., was hydrolysed

FIG. 1.



Full curve :	8-Hydroxyquinoline in alcohol.
Dash " :	" " alcoholic hydrochloric acid.
Dot and dash curve :	" " alcoholic sodium hydroxide.
Dotted curve :	8-Ethoxyquinoline in alcohol.
2 Dots and dash curve :	" " alcoholic hydrochloric acid.

at a similar dilution. These values show that hydroxyquinoline is rather weaker than aniline as a base, and is considerably less acidic than phenol.

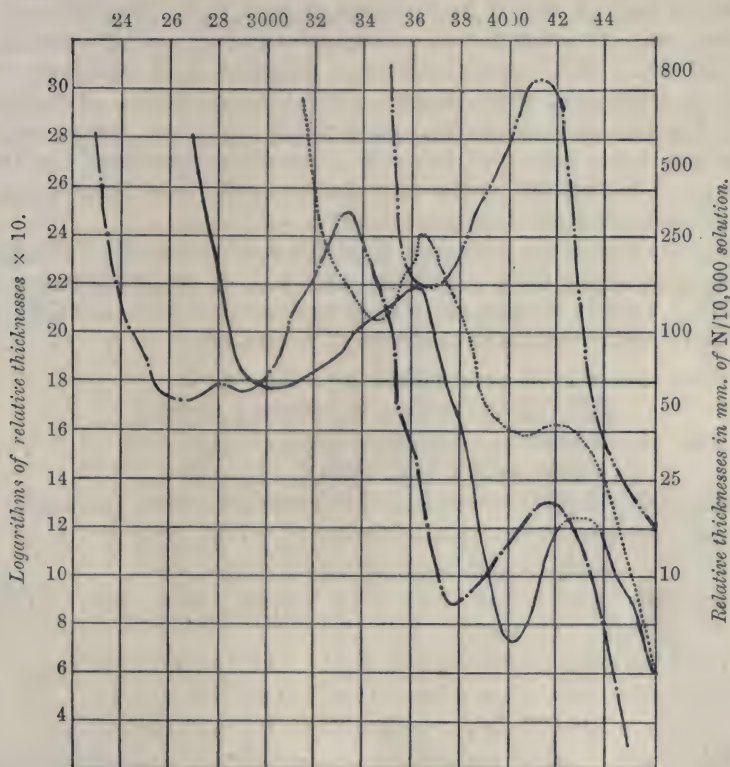
EXPERIMENTAL.

The salts of 8-hydroxyquinoline with metals were prepared by dissolving the phenol in the theoretical quantity of aqueous sodium hydroxide, and adding to this solution a neutral solution of the

acetate of the base. Instead of the acetates, solutions of the chlorides were sometimes used, to which sodium acetate in excess was added. No difference appeared to result in the product from adding excess of either solution; but when the acetate solution was in excess, the flocculent precipitate in most cases set after some

FIG. 2.

Oscillation frequencies.



Full curve: 5:7-Dibromo-8-hydroxyquinoline in alcohol.
 Dot and dash curve: " " " " alcoholic sodium
 Dotted curve: 8-Hydroxytetrahydroquinoline in alcohol. [hydroxide.
 2 Dots and dash curve: " " in alcoholic hydrochloric acid.

time to a crystalline mass of needles. The precipitates were collected, washed with water, and then dried in the air at the ordinary temperature. Copper, cadmium, and nickel yielded salts which possessed a green shade; the salts of silver, lead, zinc, and manganese were bright yellow, and those of cobalt, barium, calcium, and magnesium were buff coloured. The chromium salt was yellow on

being freshly precipitated, but could not be obtained free from excess of hydroxyquinoline. As regards the silver salt, Vis (*J. pr. Chem.*, 1892, [ii], **45**, 530) states that he obtained the salt from concentrated solutions as a green, crystalline mass, which, however, was not of constant composition. Vis gives the probable composition of the silver salt as $\text{AgC}_9\text{H}_6\text{ON} \cdot \text{C}_9\text{H}_6\text{NOH}$. I find that when the salt is precipitated as described above, it is bright yellow when fresh, but rapidly turns green in the light, and after collection, washing, and drying, it had become green almost throughout the whole mass. It yields figures on analysis agreeing with the formula $\text{AgC}_9\text{H}_6\text{ON}$. The copper salt was prepared and described by Skraup (*Monatsh.*, 1883, **3**, 540). All the dried salts, on boiling with benzene and chloroform, gave yellow solutions, which, after filtration from excess of the salt, showed the reactions for the metals. The lead salt appeared to be most soluble in benzene, and all of them were practically insoluble in water.

Before analysis the salts were dried for one hour at 100° , it being found that under these conditions the water of crystallisation was expelled, and no appreciable loss of hydroxyquinoline resulted.

The following results were obtained on analysis:

Silver salt—0.2156 gave 0.0920 Ag. Ag=42.7.

$\text{C}_9\text{H}_6\text{ONAg}$ requires Ag=42.85 per cent.

Lead salt—0.2460 lost 0.0122 on drying. $\text{H}_2\text{O}=5.0$.

0.2290 gave 0.1318 PbSO_4 . Pb=39.3.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Pb}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=5.2$; Pb=39.65 per cent.

Cadmium salt—0.2492 gave 0.0905 CdS. Cd=28.3.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Cd}$ requires Cd=28.1 per cent.

Zinc salt—0.3312 lost 0.0214 on drying, and gave 0.1346

$\text{Zn}_2\text{P}_2\text{O}_7$. $\text{H}_2\text{O}=6.5$; Zn=17.4.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Zn}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=7.1$; Zn=17.2 per cent.

Magnesium salt—0.2964 gave 0.0378 MgO . Mg=7.7.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Mg}$ requires Mg=7.8 per cent.

Cobalt salt—0.3124 lost 0.0220 on drying, and gave 0.0480 Co.

$\text{H}_2\text{O}=7.0$; Co=15.4.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Co}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=7.2$; Co=15.8 per cent.

Manganese salt—0.2812 lost 0.0166 on drying, and gave 0.0580

Mn_3O_4 . $\text{H}_2\text{O}=5.9$; Mn=14.9.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Mn}, \text{H}_2\text{O}$ requires $\text{H}_2\text{O}=5.0$; Mn=15.2 per cent.

Calcium salt—0.2482 anhydrous salt gave 0.0424 CaO . Ca=12.5.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Ca}$ requires Ca=12.2 per cent.

Barium salt—0.2470 anhydrous salt gave 0.1346 BaSO_4 .

Ba=32.0.

$(\text{C}_9\text{H}_6\text{ON})_2\text{Ba}$ requires Ba=32.3 per cent.

The water of crystallisation in the barium and calcium salts varied with the temperature of precipitation from three to four molecules of water per molecule of salt, and similar but slight variations were observed in some of the other salts. The nickel salt could not be obtained pure, the percentage of nickel found being only about one-half of the amount required. Determinations of the nitrogen in the case of the magnesium and barium salts showed that the required amount of hydroxyquinoline was present.

Hydrolysis of Salts.—The degree of hydrolysis was found by the method of Farmer (Trans., 1901, **79**, 863) and Farmer and Warth (Trans., 1904, **85**, 1713).

An attempt was made to determine the rate of inversion of sucrose by the neutral hydrochloride, but owing to the deep colour of the solution the polarimeter readings could not be taken satisfactorily, and the rate of inversion in 0.1*N*-solutions was found to be too slow in practice. The first series of determinations by Farmer and Warth's method did not yield concordant results, since it was very difficult to prevent loss of hydroxyquinoline hydrochloride on drying. The modification used by Flürscheim (this vol., p. 95), whereby the hydroxyquinoline was determined as picrate in presence of a large excess of picric acid, gave satisfactory results, a preliminary determination showing that it was an accurate method of determining hydroxyquinoline dissolved in benzene. Instead of using 1000 c.c. of water, it was more convenient to use 300 c.c. and 50 c.c. of benzene. The determinations were made at 18° by first shaking the bottle continuously for six hours at 19° to 20°, and then keeping at 18° in a thermostat for one hour, shaking occasionally. The distribution coefficient varied with the amount of hydroxyquinoline taken (about 0.3 gram) between 76 and 81, the mean value of 78.5 being taken. These variations are to some extent due to the experimental errors, as titration of the hydroxyquinoline in the aqueous layer by means of bromine water gave numbers agreeing with the amount obtained by difference in the usual way. It may be assumed that on account of its small solubility, 8-hydroxyquinoline dissolved in water is not associated, and it is probably not associated in benzene, as was shown by Auwers and Innes for ortho-substituted phenols (*Zeitsch. physikal. Chem.*, 1895, **18**, 895; 1897, **23**, 449).

The first determination with the sodium salt was made by dissolving sodium in water, taking precautions to prevent access of carbon dioxide; but it gave the same results as sodium hydroxide, purified by alcohol. The letters used below are in the same sense as those of Farmer and Warth's.

Hydrolysis of 8-Hydroxyquinoline Hydrochloride.

Concentration of hydroxyquinoline.	Concentration of acid.	Hydroxyquinoline obtained from 30 c.c. benzene.	Concentration of free base in aqueous layer.	Degree of hydrolysis.	Dilution.
c_2 .	c_1 .	gram.			
1. 0.01	0.0115	0.0230	6.73×10^{-5}	0.0416	100
2. 0.01	0.01	0.0348	1.02×10^{-4}	0.0404	100

Hydrolysis of Sodium Salt of Hydroxyquinoline.

Concentration of hydroxyquinoline.	Concentration of base.	Hydroxyquinoline obtained from 30 c.c. benzene.	Concentration of free hydroxyquinoline in aqueous layer.	Degree of hydrolysis.	Dilution.
c_2 .	c_1 .	gram.			
1. 0.01	0.0106	0.0858	2.51×10^{-4}	0.118	100
2. 0.01	0.0150	0.0554	1.62×10^{-4}	0.115	100

Aniline hydrochloride at dilution 32 and 25° is hydrolysed to the extent of 2.65 per cent. (Farmer and Warth, *loc. cit.*), which calculated to dilution 100 from the ordinary dilution formula,

$$\frac{x^2}{(1-x)v} = k, \text{ is } 4.35 \text{ at } 25^\circ; \text{ hence } 8\text{-hydroxyquinoline hydro-}$$

chloride is not very much more hydrolysed than aniline hydrochloride, taking into consideration the different temperatures. Walker showed from conductivity measurements (*Zeitsch. physikal. Chem.*, 1889, **4**, 319) that the hydrolysis of aniline and quinoline hydrochloride differed but slightly, quinoline being somewhat less hydrolysed. The presence of the hydroxyl group in 8-hydroxyquinoline has therefore little effect on the basic properties of the quinoline. This, however, does not apply to the effect of the basic character on the acidic nature of 8-hydroxyquinoline, for the degree of hydrolysis of the sodium salt at 18° is 11.6 per cent., compared with 8.8 at 25° for phenol (Hantzsch, *Ber.*, 1899, **32**, 3084), and Walker's value of 3.0 for 0.1*N* (*Zeitsch. physikal. Chem.*, 1900, **32**, 137).

Absorption Spectra.—Kahlbaum's 8-hydroxyquinoline recrystallised from alcohol and light petroleum was used. The pure substance melted at 75.8°. The band of which the head is at $1/\lambda$ 3200 about is similar in character and persistency to the band observed by Dobbie and Hartley in the case of carbostyryl (*Trans.*, 1899, **75**, 640), but with 8-hydroxyquinoline it is much wider. This similarity suggests that 8-hydroxyquinoline may partly form an internal salt, the imino-ketonic structure attributed to carbostyryl being inadmissible in this case. The salts give spectra similar in character to that of 8-hydroxyquinoline, but as the bands extend from about $1/\lambda$ 2500 these solutions are coloured. It was observed

that the faint bands of small persistency were given by the salts, and this may be due to the presence of hydrolysed salt, for the degree of hydrolysis at $N/10,000$, calculated from the values found above for $N/100$, is almost 70 per cent. Large excess of sodium hydroxide and hydrochloric acid was used in all cases, but with this degree of hydrolysis some hydrolysed salt may still persist.

5·7-Dibromo-8-hydroxyquinoline (m. p. 196°) was examined to ascertain the effect of loading the molecule, but, although the whole curve is displaced towards the red, the displacement is insufficient to produce a coloured substance. The sodium salt in this case also exhibits the faint band of small persistency referred to above. 8-Ethoxyquinoline (b. p. $285-287^{\circ}$ at 718 mm., according to Fischer and Renouf, *Ber.*, 1883, **16**, 717), boiling at $290-291^{\circ}/754$ mm., gave curves for the spectrum similar to 8-hydroxyquinoline, so that for the greater part 8-hydroxyquinoline must possess a structure similar to 8-ethoxyquinoline. The curve for the hydrochloride exhibits displacement towards the red.

8-Hydroxy-1:2:3:4-tetrahydroquinoline (m. p. $122\cdot5^{\circ}$), prepared according to Fischer and Bedall's method (*Ber.*, 1881, **14**, 1368), gave an absorption curve which differs considerably from the curves for the other compounds. The slight band at about $1/\lambda 4060$ was obtained from two different preparations, and the displacement due to salt formation was towards the ultra-violet, similar to that observed with toluidine. The spectrum of the sodium salt could not be taken, because the addition of sodium hydroxide to hydroxytetrahydroquinoline results in the production of a brown solution after a short time.

The alteration in the position of the bands due to salt formation in all the above compounds resembles that observed by Hartley in the case of quinoline and tetrahydroquinoline (*Trans.*, 1885, **47**, 685), the hydroxytetrahydroquinoline in the presence of hydrochloric acid behaving as was to be expected, like an alkylated aniline.

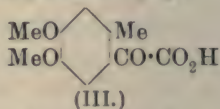
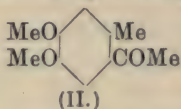
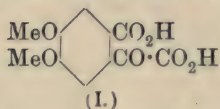
The phenolic character of 8-hydroxyquinoline cannot altogether account for the shift of the band towards the red (see Baly and Ewbank, *Trans.*, 1905, **87**, 1347) in the presence of sodium hydroxide, because the addition of hydrochloric acid causes a similar alteration.

XCIV.—*Synthesis of 6-Carboxy-3:4-dimethoxyphenylglyoxylic Acid.*

By VICTOR JOHN HARDING and CHARLES WEIZMANN.

AMONG the products of the oxidation of trimethylbrazilin by means of warm potassium permanganate, there was found to occur a dibasic acid possessing the empirical formula $C_{11}H_{14}O_9$. This acid, which was isolated and investigated in these laboratories by W. H. Perkin, jun., was shown to be 6-carboxy-3:4-dimethoxyphenylglyoxylic acid (I) ["dimethoxycarboxybenzoylformic acid"] (Trans., 1902, **81**, 1022).

In the present communication the authors describe the synthesis of this acid from 4:5-dimethoxy-o-methylacetophenone (II):



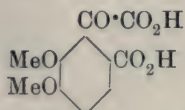
This ketone is easily prepared by the condensation of acetyl chloride and homocatechol dimethyl ether by means of aluminium chloride. When oxidised by warm potassium permanganate there is first isolated 4:5-dimethoxy-o-tolylglyoxylic acid (III). Further oxidation converts the methyl group into a carboxy-group, and leads to the production of 6-carboxy-3:4-dimethoxyphenylglyoxylic acid.

Although it has not been found possible directly to compare the synthetical acid with that obtained from trimethylbrazilin, the authors do not think there can be much doubt as to their identity. The following are the properties of the synthetical acid:

1. Calcium chloride, with a neutral solution of the ammonium salt, gives no precipitate in the cold, but on warming, the crystalline calcium salt separates at once.
2. The acid, separated by means of the calcium salt, crystallises with two molecules of water in small, brown, soluble prisms.
3. The silver salt is derived from the anhydrous acid.
4. The melting point of a specimen of acid dried in the water-oven was found to be 148° (Perkin gives 150°).

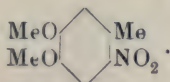
With the exception of the slight difference in the melting point, these properties agree exactly with those described by Perkin (*loc. cit.*). As, however, a difference was found between the oxime of the synthetical acid and that obtained by Perkin, it was judged necessary to convert the synthetical product into some derivative which would determine absolutely the position of the oxalyl group,

because it is easily conceivable that an acid possessing the constitution:



might show properties almost identical with the isomeric acid, as, indeed, is shown in the case of the two similarly isomeric hemipinic acids. In order to determine this point, the 6-carboxy-3:4-dimethoxyphenylglyoxylic acid was converted into *m*-hemipinic acid. This was accomplished by the distillation of the silver salt, by which method a quantitative yield of *m*-hemipinic anhydride was obtained. This proves beyond all doubt the constitution of the synthetical acid, and establishes its identity with the acid obtained by the oxidation of trimethylbrazilin.

4:5-Dimethoxy-*o*-methylacetophenone, when warmed in glacial acetic acid solution with a few drops of concentrated nitric acid, undergoes a remarkable reaction; the acetyl group is displaced by a nitro-group, with the production of nitrohomocatechol dimethyl ether:



The displacement of a carboxy-group by a nitro-group is well known, and Salway (Trans., 1909, **95**, 1155) has shown that the aldehyde group can also be displaced by a nitro-group. The displacement of an acetyl group by a nitro-group, however, does not seem to have been previously observed, and it is hoped shortly to communicate the results of investigations in this direction. It is worthy of note that the displacement of the acetyl group can be effected by warm dilute aqueous nitric acid, the temperature of the reaction and concentration of the acid apparently having very little influence on the displacement.

EXPERIMENTAL.

4:5-Dimethoxy-*o*-methylacetophenone, $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_2 \cdot \text{COMe}$.

This ketone is easily obtained by condensing acetyl chloride (30 grams) with homocatechol dimethyl ether (50 grams), dissolved in 200 c.c. of carbon disulphide, by means of aluminium chloride (100 grams). The reaction is maintained at the ordinary temperature for twenty-four hours, when it is heated for a further two hours on the water-bath. The dark red product is decomposed by water, and the carbon disulphide removed by distillation in a current of steam. The dark brown residual oil is then

extracted by means of ether, washed with a dilute solution of potassium hydroxide, dried, and distilled. The ketone, which distils at $204^{\circ}/70$ mm., rapidly solidifies in the receiver, and is purified by crystallisation from methyl alcohol or light petroleum of high boiling point:

0.1409 gave 0.3503 CO_2 and 0.0941 H_2O . $\text{C}=67.7$; $\text{H}=7.4$.

$\text{C}_{11}\text{H}_{14}\text{O}_3$ requires $\text{C}=68.0$; $\text{H}=7.3$ per cent.

4: 5-Dimethoxy-o-methylacetophenone crystallises in short, colourless needles, melting at 68° . It possesses an aromatic odour, recalling that of homocatechol dimethyl ether.

The phenylhydrazone, prepared in the usual way, crystallises from acetic acid. It shrinks together at 168° , and decomposes at 170° :

0.2020 gave 18.5 c.c. N_2 (moist) at 17° and 725 mm. $\text{N}=10.1$.

$\text{C}_{17}\text{H}_{20}\text{O}_2\text{N}_2$ requires $\text{N}=9.9$ per cent.

The semicarbazone decomposes at 186° .

Piperonylidene-4: 5-dimethoxy-o-methylacetophenone,
 $\text{C}_6\text{H}_2\text{Me}(\text{OMe}_2) \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_3 : \text{O}_2 : \text{CH}_2$.

This derivative is prepared by dissolving molecular quantities of 4: 5-dimethoxy-o-methylacetophenone and piperonal in methyl alcohol, adding a few drops of 50 per cent. aqueous potassium hydroxide, and boiling for a short time. On dilution with water, the resulting oil solidifies after some time. This is collected and crystallised from alcohol, from which it separates in golden-yellow needles, melting at $108\text{--}109^{\circ}$:

0.1152 gave 0.2916 CO_2 and 0.0602 H_2O . $\text{C}=69.1$; $\text{H}=5.8$.

$\text{C}_{19}\text{H}_{18}\text{O}_5$ requires $\text{C}=69.6$; $\text{H}=5.5$ per cent.

Oxidation of 4: 5-Dimethoxy-o-methylacetophenone by means of Alkaline Potassium Permanganate.

A.—*Formation of 4: 5-Dimethoxy-o-tolylglyoxylic Acid*,
 $\text{C}_6\text{H}_2\text{Me}(\text{OMe})_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$.

Ten grams of 4: 5-dimethoxy-o-methylacetophenone are added to 8 grams of sodium carbonate dissolved in 100 c.c. of water, and heated on the water-bath. Sixty grams of potassium permanganate, dissolved in 600 c.c. of water, are then added. The oxidation proceeds slowly. When the pink colour of the permanganate has disappeared, the manganese dioxide is collected, washed several times with boiling water, and the combined filtrates are evaporated to a small bulk on the water-bath. On acidifying with hydrochloric acid, 4:5-dimethoxy-o-tolylglyoxylic acid gradually crystallises out. After recrystallisation from hot water, it melts at 155° :

0.1130 gave 0.2434 CO_2 and 0.0520 H_2O . $\text{C}=58.8$; $\text{H}=5.1$.

$\text{C}_{11}\text{H}_{12}\text{O}_5$ requires $\text{C}=58.9$; $\text{H}=5.3$ per cent.

4: 5-Dimethoxy-o-tolylglyoxylic acid crystallises from water in short needles, and is insoluble in cold benzene. Its solution in concentrated sulphuric acid develops a cherry-red colour.

B.—*Synthesis of 6-Carboxy-3:4-dimethoxyphenylglyoxylic Acid*,
 $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$.

This acid is obtained by the oxidation of 4: 5-dimethoxy-o-methylacetophenone under the following conditions. The ketone (20 grams) is added to sodium carbonate (15 grams) dissolved in water (100 c.c.), and a 10 per cent. solution of potassium permanganate (150 grams) added gradually, the operation being conducted on the water-bath. When the oxidation is complete, the manganese dioxide is collected, extracted several times with boiling water, and the combined filtrates and washings are evaporated to a very small bulk, acidified with hydrochloric acid, mixed with sand, and then evaporated to complete dryness. The dry mass is then extracted by means of ether in a Soxhlet apparatus, and on evaporating the ethereal extract a viscid liquid is obtained, which crystallises after some time. The silver salt was prepared for analysis, and, as observed by Perkin (Trans., 1902, **81**, 1023), is derived from the anhydrous acid. (Found, $\text{C}=28.2$; $\text{H}=1.7$; $\text{Ag}=45.8$. Calc., $\text{C}=28.2$; $\text{H}=1.7$; $\text{Ag}=46.1$ per cent.) In order to prepare an acid corresponding exactly in properties with that described by Perkin (*loc. cit.*), a portion of the crude oily acid, obtained direct from the oxidation, was dissolved in water, neutralised with ammonia, and boiled with a solution of calcium chloride. The calcium salt, which separated during the heating, was collected and decomposed by hydrochloric acid, when, after some time, the 6-carboxy-3:4-dimethoxyphenylglyoxylic acid crystallised in small, brown prisms. These were collected and dried on porous porcelain in the air for twenty-four hours. (Found, $\text{C}=45.0$; $\text{H}=4.5$. Calc., $\text{C}=45.5$; $\text{H}=4.8$ per cent.) When dried in the water-oven for a further two hours, the acid melted at 148° (Perkin gives 150°). The acid dissolves in concentrated sulphuric acid with a yellow colour, gradually deepening to a reddish-orange. When dissolved in benzene (containing thiophen) and concentrated sulphuric acid added, the characteristic deep green colour due to glyoxylic acids slowly makes its appearance. In order to satisfy ourselves of the identity of the acid obtained from the calcium salt with that obtained by direct crystallisation from ether (see above), we converted both into their oximes (see p. 1130), which were found to be identical.

*Distillation of the Silver Salt of 6-Carboxy-3:4-dimethoxyphenylglyoxylic Acid.**Production of m-Hemipinic Anhydride.*

0.5 Gram of the silver salt of 6-carboxy-3:4-dimethoxyphenylglyoxylic acid is placed in an ignition tube held mouth downwards, and gently heated. The salt slowly decomposes, the *m*-hemipinic anhydride distils, and condenses halfway down the tube. The product was identified by dissolving in warm aqueous potassium hydroxide, acidifying, extracting with ether, and converting the *m*-hemipinic acid formed into its characteristic ethylimide. The latter, after one crystallisation from alcohol, melted sharply at 227° , thus proving that *m*-hemipinic acid and not *o*-hemipinic acid had been formed.

Oxime of 6-Carboxy-3:4-dimethoxyphenylglyoxylic Acid.

In investigating the action of hydroxylamine on 6-carboxy-3:4-dimethoxyphenylglyoxylic acid, the authors have obtained results differing from those of Perkin (Trans., 1902, **81**, 1024), who found that the product of the reaction was a substance, $C_{22}H_{21}O_{14}N$, which he suggested might be a compound of one molecule of the oxime of 6-carboxy-3:4-dimethoxyphenylglyoxylic acid with one molecule of unchanged acid. The authors, however, have succeeded in obtaining the normal oxime.

The crude acid (2 grams) was dissolved in a solution of potassium hydroxide (4 grams) in 20 c.c. of water, hydroxylamine hydrochloride (2 grams) added, and the whole kept for twenty-four hours. The liquid was then acidified and extracted fifteen times with fresh quantities of ether. On evaporating the ethereal solution, the oxime rapidly separated in white masses. It was collected, washed with fresh ether, and dried in a vacuum. When heated in a capillary tube, it passes at 134° with a faint explosion into a yellow solid, which does not melt at 220° . It can be crystallised from a very small amount of water, from which it separates in long, slender needles, and these show the same characteristic properties on heating. It is extremely insoluble in ether:

0.1129 gave 0.2058 CO_2 and 0.0443 H_2O . $C=49.6$; $H=4.3$.

0.1434 gave 6.6 c.c. N_2 (moist) at 20° and 765 mm. $N=5.2$.

$C_{11}H_{11}O_7N$ requires $C=49.1$; $H=4.1$; $N=5.2$ per cent.

This same oxime was obtained, also, from a specimen of the acid prepared through the calcium salt (p. 1129).

From the ethereal mother liquors of the oxime there crystallised, on keeping, a small amount of a substance which formed large

plates; from water it separated in faintly yellow, oblong plates. It did not melt at 240° :

0.1367 gave 3.0 c.c. N_2 (moist) at 21° and 763 mm. $N = 2.5$ per cent.

The amount, however, was too small to permit of further investigation.

*Action of Nitric Acid on 4:5-Dimethoxy-o-methylacetophenone.
Formation of Nitrohomocatechol Dimethyl Ether.*

(a) One gram of the ketone was dissolved in 20 c.c. of acetic acid, and 2 c.c. of concentrated nitric acid added. A vigorous reaction soon commenced, the liquid becoming dark red in colour, and copious brown fumes being evolved. As soon as the violence of the reaction subsided, the product was poured into water, and the nitro-compound which separated was collected, washed with water, and crystallised from methyl alcohol. (Found, $C = 55.1$; $H = 5.4$; $N = 7.2$. Calc., $C = 54.9$; $H = 5.5$; $N = 7.1$ per cent.)

This nitro-compound crystallises from alcohol in clusters of needles, melts at 117° , and when mixed with a specimen of nitrohomocatechol dimethyl ether, prepared by the nitration of homocatechol dimethyl ether, no alteration in the melting point could be observed.

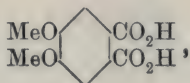
(b) Five grams of the ketone were added to 100 c.c. of dilute nitric acid (1:4), and heated on the water-bath for two hours and then on the sand-bath until almost all the oil had dissolved. On cooling, nitrohomocatechol dimethyl ether separated out, and was found to be identical with the product obtained by method (a).

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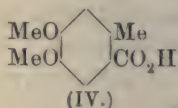
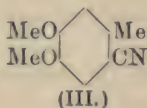
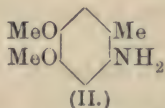
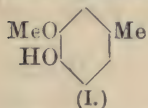
XCV.—*m-Hemipinic and Asaronic Acids.*

By BERNARD DUNSTAN WILKINSON LUFF, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

AMONG the degradation products obtained by the oxidation of the alkaloids and other natural products with permanganate, there are few substances which are so frequently met with as *m*-hemipinic acid:

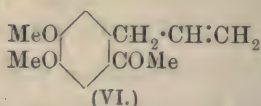
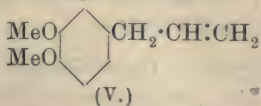


and yet, in spite of its importance, there is still great difficulty in obtaining this acid in quantity. As we were anxious to employ *m*-hemipinic acid in some synthetical experiments on which we are engaged, we undertook the present investigation in the hope of discovering a more convenient method for its preparation. The starting point selected was creosol (I), which is readily obtained in quantity, and this was methylated by means of methyl sulphate and potassium hydroxide in the usual manner. The creosol methyl ether, thus obtained, was nitrated, and the nitro-derivative reduced by tin and hydrochloric acid to 4:5-dimethoxy-*o*-toluidine (II), a crystalline substance which melts at 109°. This amino-derivative was next converted, by Sandmeyer's reaction, into 4:5-dimethoxy-*o*-toluonitrile (III), which melts at 81°, and, on hydrolysis with barium hydroxide, yields 4:5-dimethoxy-*o*-toluic acid (IV), an acid which had previously been prepared by Perkin and Weizmann (Trans., 1906, 99, 1651) by another process, namely, from the corresponding aldehyde by oxidation. At that time it was observed that *m*-hemipinic acid was also produced in small quantities, and we now find that 4:5-dimethoxy-*o*-toluic acid is quantitatively converted into *m*-hemipinic acid by oxidation with hot alkaline permanganate:



We have prepared considerable quantities of *m*-hemipinic acid in the way described above, but the process is still not convenient, principally on account of the time required to carry out the number of steps which have to be followed during the preparation.

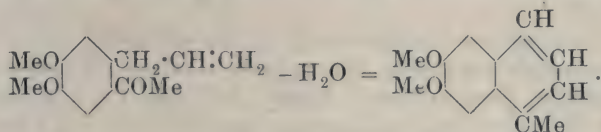
A second series of experiments was then instituted which seemed to promise well, and the starting point in this case was eugenol, $\text{MeO} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2$, which was converted into eugenol methyl ether (V), and then treated with acetyl chloride in the presence of aluminium chloride, in the hope that acetyleneugenol methyl ether (VI) would result, which, on oxidation, should readily yield *m*-hemipinic acid:



Instead, however, of this ketone, we obtained a brown, resinous substance, which did not yield a semicarbazone, and from which nothing crystalline could be obtained by the action of solvents.

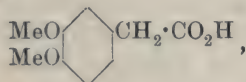
When this uninviting substance was distilled under diminished pressure, it yielded a beautifully crystalline substance, $\text{C}_{13}\text{H}_{14}\text{O}_2$,

melting at 114° , the properties of which (p. 1140) clearly prove that it is 6:7-dimethoxy-1-methylnaphthalene. The formation of this interesting substance is evidently due to elimination of water from the methyl-ketone, and this internal condensation is probably the result of the dehydrating action of the aluminium chloride:



This naphthalene derivative gives *m*-hemipinic acid on oxidation, but the process is of no value as a method of preparation.

We have also carried out experiments on the oxidation of eugenol methyl ether itself in the hope of obtaining 4:5-dimethoxyphenylacetic acid:



which we require for our synthetical experiments, but, although this acid is produced in this way, the yield is very small, owing to the fact that veratric acid is the principal product of the oxidation.

In the same way, we find that safrole, $\text{CH}_2 \cdot \text{O}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{CH}_2 \cdot \text{CH} : \text{CH}_2$, yields, on oxidation, principally piperonylic acid, only small quantities of piperonylacetic acid:



being obtained.

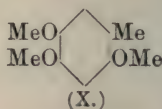
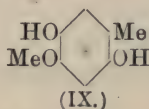
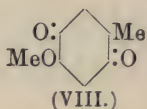
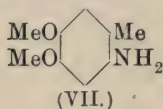
The synthesis of asaronic acid:



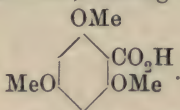
an account of which is included in this communication, was carried out as follows. We observed that 4:5-dimethoxy-*o*-toluidine (VII) is readily oxidised by ferric chloride to 4-methoxy-2:5-toluquinone (VIII),* which crystallises in golden spangles, melts at 170 – 172° , and is readily reduced by sulphurous acid to 4-methoxy-2:5-toluquinol (IX). This substance melts at 124° , and yields, on treatment with methyl sulphate and potassium hydroxide, 2:4:5-trimethoxytoluene (m. p. 55° , X), which, on oxidation with hot

* It is remarkable that the elimination of the methyl group, which is necessary for quinone formation, should take place so readily at the ordinary temperature.

alkaline permanganate, is converted, almost quantitatively, into asaronic acid:



Asaronic acid was first obtained by the oxidation of asarone, a substance which occurs in the root of *Asarum europaeum*, with permanganate (Butleroff and Rizza, *J. Russ. Phys. Chem. Soc.*, 1887, **19**, 3), and it was long thought that this acid was a derivative of phloroglucinolcarboxylic acid, having the constitution:

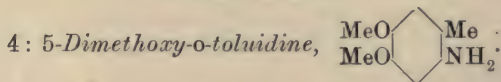


Gattermann and Eggers (*Ber.*, 1899, **32**, 289) succeeded, however, in synthesising the corresponding aldehyde from 1:2:4-trimethoxybenzene by the action of hydrogen cyanide in the presence of aluminium chloride. In this reaction, the aldehyde group always takes up the para-position with respect to a methoxy-group, and Gattermann and Eggers therefore represent the formation and constitution of the aldehyde, and therefore of asaronic acid, as follows:



The synthesis which we have described in this communication supports this view, and the constitution of asaronic acid may now be considered as definitely established.

EXPERIMENTAL.



The starting point in the preparation of this substance is creosol methyl ether, $\text{C}_6\text{H}_3\text{Me}(\text{OMe})_2$ (1:3:4), which is readily obtained in quantity by the following process. Creosol, $\text{C}_6\text{H}_3\text{Me}(\text{OMe})\cdot\text{OH}$ (1:3:4) (50 grams), is dissolved in methyl alcohol (100 c.c.), mixed with methyl sulphate (90 grams), and cooled to -10° . A solution of potassium hydroxide (75 grams) in 150 c.c. of water is then added, with vigorous shaking, when a reaction sets in, which continues for about three minutes, and is then complete. The product is extracted with ether, the extract well washed with water, dried and evaporated, and the residue distilled, when pure creosol

methyl ether is obtained in an almost quantitative yield. It distils at 218° , and, on cooling, solidifies to a crystalline mass, melting at 24° .

The nitration of creosol methyl ether (compare Cousin, *Ann. Chim. Phys.*, 1898, [vii], **13**, 545) was carried out under the following conditions.

Creosol methyl ether (40 grams) dissolved in glacial acetic acid (200 c.c.) was added to a solution of concentrated nitric acid (25 grams) in glacial acetic acid (80 c.c.), the whole being kept cold by running water. Nitration took place readily, and, after leaving for a few minutes, the product gave, on dilution with water, a mass of yellow needles of nitrocreosol methyl ether, $C_6H_2Me(OMe)_2 \cdot NO_2$ (1 : 4 : 5 : 2), which, after crystallising from alcohol, melted at 119° .

4 : 5-Dimethoxy-*o*-toluidine was obtained by reducing nitrocreosol methyl ether with tin and hydrochloric acid. The nitro-derivative (50 grams) was dissolved in hot alcohol (100 c.c.), granulated tin (70 grams) added, and then concentrated hydrochloric acid (150 c.c.) diluted with water (50 c.c.) gradually run in, and finally the whole was heated on the steam-bath for an hour. The excess of acid was partly neutralised by sodium hydroxide, the tin removed by hydrogen sulphide, and, after filtering, the filtrate was evaporated to a small bulk and rendered alkaline, when the base separated in glistening crystals, the yield being about 60 per cent. :

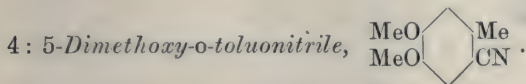
0.2238 gave 0.5323 CO_2 and 0.1600 H_2O . C = 64.8 ; H = 7.9.

$C_9H_{13}O_2N$ requires C = 64.7 ; H = 7.9 per cent.

4 : 5-Dimethoxy-*o*-toluidine crystallises from a mixture of chloroform and light petroleum in clusters of needles, melting at 109° ; it is readily soluble in ether, alcohol, or hot water, and moderately so in chloroform. The alcoholic solution gives, on the addition of ferric chloride, a beautiful blue coloration, but this gradually fades, and long, golden-yellow needles of 4-methoxy-2 : 5-toluquinone separate (p. 1137). The *acetyl* derivative was prepared by heating with acetic anhydride in the usual manner, and crystallises from water in pearly plates, melting at 141° :

0.4262 gave 24.4 c.c. N_2 at 15° and 764 mm. N = 6.8.

$C_{11}H_{15}O_3N$ requires N = 6.7 per cent.

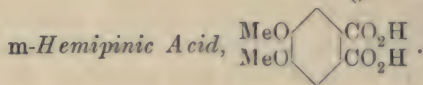
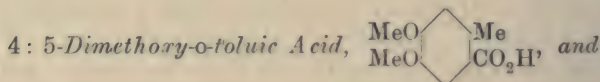


This substance was prepared from 4 : 5-dimethoxy-*o*-toluidine by the Sandmeyer reaction. The base (10 grams) was dissolved in hydrochloric acid (30 c.c.) and water (100 c.c.), and the solution

diazotised by the addition of sodium nitrite in the usual manner. The cuprous potassium cyanide solution (from 22 grams of potassium cyanide) was then added to the diazotised solution with constant shaking, and, after fifteen minutes, the whole was warmed to 80°. The product was then extracted with ether, the ethereal solution washed with sodium hydroxide, then with water, and dried. On removal of the ether, the nitrile was obtained as a crystalline mass, of which the yield was about 50 to 60 per cent. of that theoretically possible, and this crude product was employed, without further purification, for the preparation of 4:5-dimethoxy-*o*-toluic acid (see the next section). The nitrile is fairly soluble in hot water, and separates, on cooling, in silky needles, which melt at 81°:

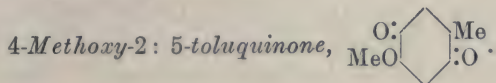
0.1532 gave 0.3806 CO₂ and 0.0876 H₂O. C=67.7; H=6.3.

C₁₀H₁₁O₂N requires C=67.8; H=6.3 per cent.



In preparing 4:5-dimethoxy-*o*-toluic acid, the crude nitrile was hydrolysed by boiling with barium hydroxide until ammonia ceased to be evolved, the product was filtered, and acidified with hydrochloric acid, when the acid was precipitated in a practically pure condition. It was identified by the fact that it melted at 145°, and that there was no alteration in melting point when it was mixed with a specimen of this acid which had been prepared by Perkin and Weizmann (Trans., 1906, **99**, 1651). The conversion of 4:5-dimethoxy-*o*-toluic acid into *m*-hemipinic acid was carried out under the following conditions. The acid was dissolved in a slight excess of sodium hydroxide in a porcelain basin, and 5 per cent. alkaline permanganate added to the boiling solution until a permanent pink colour was produced. After destroying the excess of permanganate by the addition of a little alcohol, the filtrate and washings from the manganese precipitate were acidified with hydrochloric acid and evaporated to dryness. The residue was mixed with sand and extracted with ether in a Soxhlet apparatus, when it was observed that crystals soon began to separate from the ethereal extract, and, when extraction was complete, the ether was removed by evaporation and the residue crystallised from hot water. An acid was thus obtained in shining needles, which melted at temperatures ranging from 175° to 188° according to the

rate of heating, and was identified as *m*-hemipinic acid by conversion into the ethylimide and by its other properties. The amount obtained was almost that demanded by theory, and this fact emphasises again the remarkable stability of *m*-hemipinic acid towards alkaline permanganate.



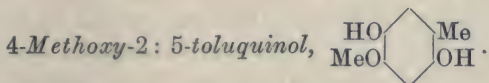
It has already been stated (p. 1135) that this interesting substance is produced when 4:5-dimethoxy-*o*-toluidine is oxidised with ferric chloride. In preparing it, a strong solution of ferric chloride is added to an aqueous solution of the hydrochloride of the base until further addition no longer produces a blue coloration.

The long needles, which separate after some time, are collected and purified by crystallisation from alcohol, from which the quinone separates in golden spangles:

0.1664 gave 0.3862 CO₂ and 0.0817 H₂O. C=63.2; H=5.4.

C₈H₈O₃ requires C=63.1; H=5.2 per cent.

4-Methoxy-2:5-toluquinone softens at about 165°, and melts and decomposes at 170—172°; it is volatile in steam, and possesses the characteristic odour of quinone. It is soluble in hot water, alcohol, or benzene, but is very sparingly so in light petroleum or ether. The solution in ether gives, on the addition of an ethereal solution of magnesium methyl iodide, a bluish-green colour, a reaction which is characteristic of quinones.



When the quinone, just described, is suspended in warm water and a stream of sulphur dioxide passed, it gradually dissolves, and, on cooling, the dihydroxy-derivative separates in colourless needles:

0.1734 gave 0.3964 CO₂ and 0.1062 H₂O. C=62.3; H=6.8.

C₈H₁₀O₃ requires C=62.3; H=6.5 per cent.

4-Methoxy-2:5-toluquinol melts at 124°, and is soluble in most organic solvents and in hot water; ferric chloride oxidises it to the quinone without the production of any characteristic coloration.

2:4:5-Trimethoxytoluene, C₆H₂Me(OMe)₃, is prepared by methylating the dihydroxy-derivative just described. The substance (20 grams) is dissolved in methyl alcohol (75 c.c.), methyl sulphate (70 grams) is added, and, after the whole has been cooled to -10°, a solution of potassium hydroxide (60 grams) in water (120 c.c.) is added, when a vigorous reaction sets in. As soon as

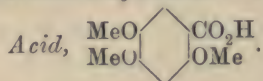
this has subsided, the product is extracted with ether, the ethereal solution washed, dried, and evaporated, when the trimethoxy-derivative remains as a syrup, which, on rubbing with a glass rod, soon solidifies:

0.1662 gave 0.4022 CO_2 and 0.1170 H_2O . $\text{C}=65.9$; $\text{H}=7.8$.

$\text{C}_{10}\text{H}_{14}\text{O}_3$ requires $\text{C}=65.9$; $\text{H}=7.7$ per cent.

2:4:5-Trimethoxytoluene melts at 55° , and crystallises from dilute methyl alcohol in leaflets; it is readily soluble in ether, alcohol, or light petroleum.

Oxidation of 2:4:5-Trimethoxytoluene: Formation of Asaronic



The oxidation of 2:4:5-trimethoxytoluene to asaronic acid was carried out under the following conditions. The finely-powdered substance (2 grams) was suspended in water (50 c.c.), heated to boiling, and a 5 per cent. alkaline solution of permanganate gradually added until the pink colour remained after boiling for three minutes. The slight excess was removed by the addition of alcohol, the filtrate and washings of the manganese precipitate acidified with hydrochloric acid until just acid to Congo-paper, and evaporated to dryness. The residue, mixed with sand, was extracted with ether in a Soxhlet apparatus, and in this way a colourless, crystalline acid was obtained, which separated from a mixture of light petroleum and benzene in glistening needles, melting at 143° . That this substance was asaronic acid was proved by adding a little nitric acid to its solution in glacial acetic acid and warming gently; effervescence set in, due to the evolution of carbon dioxide, and, on cooling, a pale yellow, crystalline solid separated, which melted at 130° and exhibited all the properties of 5-nitro-1:2:4-trimethoxybenzene (compare Fabinyi and Széki, *Ber.*, 1906, **39**, 3681).

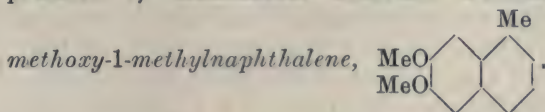
Oxidation of Eugenol Methyl Ether.

Eugenol methyl ether, $[3:4](\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2$, and *iso*-eugenol methyl ether, $[3:4](\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{CH}\cdot\text{CH}_3$, are readily prepared in almost quantitative yields by methylation with methyl sulphate in the way described in detail in the case of the preparation of the methyl ether of creosol (p. 1135). The oxidation of the methyl ether of eugenol was investigated in the hope of readily obtaining dimethoxyphenylacetic acid, $[3:4](\text{MeO})_2\text{C}_6\text{H}_3\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, a substance of considerable importance in connexion with our synthetical researches on the alkaloids. The best results were obtained under the following conditions. Eugenol

methyl ether (30 grams) was dissolved in acetone (250 c.c.), the solution cooled in ice, and gradually treated with a cold saturated solution of permanganate (100 grams), when oxidation proceeded slowly at first, but afterwards more rapidly.

The filtrate from the manganese precipitate, after distilling off the acetone and concentrating somewhat on the water-bath, gave, on acidifying, a large quantity of a yellowish-brown precipitate, which was readily identified as veratric acid. The filtrate from this was concentrated and extracted with ether, and the ethereal extract shaken with sodium carbonate. The alkaline solution was boiled with animal charcoal, filtered, cooled in ice, and acidified, when a crystalline precipitate gradually separated, and the separation was much facilitated by rubbing the sides of the vessel with a glass rod. After crystallisation from water, the acid melted at 97° , and proved to be dimethoxyphenylacetic acid, but the yield was unsatisfactory, and seldom more than 4 to 5 grams from 30 grams of eugenol methyl ether. A similar process of oxidation applied to safrole, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{:CH:CH}_2$, yielded a mixture of piperonylic acid and piperonylacetic acid, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_3\text{:CH}_2\text{:CO}_2\text{H}$, the latter being again produced in comparatively small quantity.

The Action of Acetyl Chloride on Eugenol Methyl Ether in the presence of Aluminium Chloride. Formation of 6:7-Di-



This interesting formation of a naphthalene derivative takes place under the following conditions. Eugenol methyl ether (30 grams), dissolved in carbon disulphide (50 c.c.) in a reflux apparatus, is mixed with powdered aluminium chloride (30 grams), and then acetyl chloride (16 grams), dissolved in an equal volume of carbon disulphide, is gradually added. The reaction becomes more vigorous as the acetyl chloride is added, and, when it has subsided, the product is heated on the steam-bath for one hour. The carbon disulphide is then decanted, and the residual aluminium compound decomposed by crushed ice and water, and, after adding 15 c.c. of concentrated hydrochloric acid, a current of steam is passed for about five minutes.

The whole is then extracted with ether, the ethereal solution washed with water, then with sodium hydroxide, dried, and the ether evaporated. Since the residue did not crystallise, and an attempt to prepare a semicarbazone was unsuccessful, it was distilled under 18 mm. pressure, when a considerable quantity passed over at $180\text{--}190^{\circ}$ and again at $190\text{--}220^{\circ}$, a resinous mass being left.

On long standing, the two fractions deposited a crystalline substance, which was freed from oily impurity by contact with porous porcelain and then crystallised from alcohol, from which pearly leaflets, melting at 114° , separated:

0.1828 gave 0.5152 CO_2 and 0.1177 H_2O . $\text{C}=76.9$; $\text{H}=7.1$.

$\text{C}_{13}\text{H}_{14}\text{O}_2$ requires $\text{C}=77.2$; $\text{H}=6.9$ per cent.

In a determination of the molecular weight by the cryoscopic method:

0.177, in 17.8 c.c. benzene, gave $\Delta t = -0.255^{\circ}$. $\text{M.W.}=195$.

$\text{C}_{13}\text{H}_{14}\text{O}_2$ requires $\text{M.W.}=202$.

The following properties of the substance clearly indicate that it is 6:7-dimethoxy-1-methylnaphthalene.

I. The substance was treated with concentrated nitric acid in glacial acetic acid solution; on dilution with water a nitro-derivative was precipitated, which was then reduced with tin and hydrochloric acid. The product was rendered alkaline, extracted with ether, and the oil obtained dissolved in hydrochloric acid and treated with sodium nitrite. The resulting diazo-solution, added to an alkaline solution of β -naphthol, yielded a blood-red dye, which turned blue on the addition of concentrated sulphuric acid, and the solution became red on dilution. These colour changes are characteristic of solutions of naphthalene azo-derivatives.

II. The substance was heated with hydriodic acid, extracted with ether, and the residue, obtained after evaporating off the ether, dissolved in alcohol and mixed with ferric chloride. A blue colour was produced, showing that the substance is a naphthol derivative, and not merely a derivative of catechol.

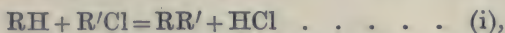
III. The substance yields *m*-hemipinic acid on oxidation. In this experiment, the crude substance (20 grams) was employed, and this was dissolved in acetone (200 c.c.) and oxidised with 5 per cent. permanganate solution and some potassium carbonate in a stoppered bottle on the shaking machine. When the pink colour remained permanent, the excess of permanganate was removed by sodium sulphite, and the filtrate from the manganese precipitate acidified with hydrochloric acid and evaporated to dryness. The residue, mixed with sand, was extracted in a Soxhlet apparatus, and the extract boiled with water and animal charcoal, filtered, and concentrated, when glistening needles separated, which melted at about 178° , and were easily identified as *m*-hemipinic acid.

The authors wish to state that much of the expense of this investigation was covered by a grant from the Chemical Society.

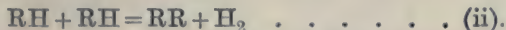
XCVI.—*The Friedel-Crafts' Reaction Applied to Naphthalene. The Action of Di-, Tri-, and Tetra-alkyl Halides. Preparation of $\alpha\beta\alpha'\beta'$ -Dinaphthanthracene.**

By ANNIE HOMER, B.A. (Fellow of Newnham College, Cambridge).

A STUDY of the literature dealing with the applications of the Friedel-Crafts' reaction to mixtures of naphthalene with the di-, tri-, and tetra-halogen derivatives of methane and ethane reveals the existence of many contradictory statements and of much fragmentary data. As the development of the author's previous work (Trans., 1907, **91**, 1103) necessitated the use of this reaction, a revision and extension of much of the published work was undertaken. Whilst the typical course of the reaction is represented by the equation :



it was observed that when naphthalene is used, this reaction is accompanied by others, a discrepancy which is explained by reference to the demonstration by Friedel and Crafts (*Compt. rend.*, 1885, **100**, 692) that when aluminium chloride acts on benzene, toluene, or naphthalene alone, condensation occurs in accordance with the equation :



The work about to be described shows that in the condensation of an aromatic hydrocarbon with a halogen derivative of a paraffin, reactions (i) and (ii) occur simultaneously, the difference between the reaction velocities being greatly affected by the temperature. But whilst with benzene and its homologues reaction (ii) proceeds with a negligibly small velocity below 160°, with naphthalene it occurs to an appreciable extent even at 80°, and at higher temperatures becomes the main reaction.

The concordant results of previous investigators have shown that the alkyl halides react with naphthalene and aluminium chloride according to equation (i), the only exception being methyl chloride, which the author of this paper has investigated. The present work is therefore confined to the condensation of the hydrocarbon with (a) *as*-dichloroethane, (b) methylene chloride, (c) ethylene bromide, (d) chloroform, (e) *s*-tetrachloro- and tetrabromo-ethane, and (f) nickel carbonyl. The condensation (e) was of special importance as promising a means of obtaining the dinaphthanthracene, $C_{22}H_{14}$,

* This paper corresponds with the two abstracts in Proc., 1910, **26**, 11, 12.

prepared by Hartenstein (*Diss.*, Jena, 1892), a specimen of this substance being required for the study of its absorption spectrum in connexion with the investigation of the constitution of the tetramethylpicene previously prepared by the author (Homer and Purvis, *Trans.*, 1908, **93**, 1319); eventually Prof. E. von Meyer kindly supplied a specimen of Hartenstein's preparation.

The condensations described in the present paper were performed in each case by treating the mixture of paraffin halogen compound and naphthalene, in theoretical proportion, with aluminium chloride not exceeding in weight 20 per cent. of the naphthalene used. Since it was soon found that rise in temperature in the initial stages favours reaction (ii) and leads to the production of $\beta\beta$ -dinaphthyl, the condensation, whenever possible, was allowed to proceed in the cold for one or two days; the tarry product, after being heated for one and a-half hours to the boiling point of the alkyl halide, while still hot was treated with hydrochloric acid and water. After half an hour the mass was extracted with benzene and the solvent separated from the extract by distillation; the residues were then fractionally distilled under (A) ordinary and (B) diminished pressure, and the fractions systematically examined as indicated below.

(a) *Interaction of as-Dichloroethane and Naphthalene.*

From the products of this reaction, Bodroux (*Bull. Soc. chim.*, 1901, [iii], **25**, 491) isolated the α - and β -methyl- and ethylnaphthalenes and $\beta\beta$ -dinaphthyl. The violence of the reaction, which sets in immediately, has to be modified by adding the aluminium chloride gradually and by external cooling.

In the present work it has been shown that:

(A) *Distillation under ordinary pressure* yielded three fractions: *Fraction i* consisted of naphthalene.

Fraction ii gave on redistillation a portion boiling at 243—245°. The crystals deposited from this solution on cooling yielded a picrate melting at 114° when crystallised from benzene, and at 110° when crystallised from alcohol, the analysis of which showed it to be the β -methylnaphthalene obtained by Bodroux.

Fraction iii, which distilled at the temperature at which the glass began to soften, was obtained as a dark viscous oil, giving a crystalline deposit, which, after washing with petroleum and crystallisation from benzene, melted at 180—182°; analysis of the picrate which melted at 183° showed this substance to be $\beta\beta$ -dinaphthyl. It was observed that during the distillation of the products of the reaction active decomposition was taking place, a fact not noted by Bodroux.

(B) *Distillation under diminished pressure* yielded three fractions.

Fraction i (below 250°/20 mm.) yielded on redistillation under 760 mm. pressure naphthalene and a little of an oil boiling at 240—260°; the oil was probably a mixture of methylnaphthalenes, and was not further examined.

Fraction ii (250°/20 mm.) was a highly fluorescent oil the production of which had been noted by Bodroux, who, however, did not attempt to isolate any pure substance from it. After repeated distillation and long keeping, this oil solidified completely, and on repeated crystallisation from hot alcohol colourless, non-fluorescent needles melting at 90·5° were obtained, which agrees closely with the melting point of dinaphthylmethane, given as 92° (Richter, *Ber.*, 1880, **13**, 1728). The fluorescent oil and the crystals had the same composition, as shown by the corresponding analyses I and II:

I. 0·2903 gave 0·9938 CO₂ and 0·1635 H₂O. C=93·38; H=6·31.

II. 0·1036 „ 0·3548 CO₂ „ 0·0597 H₂O. C=93·42; H=6·47.

M.W. by cryoscopic method in benzene=255·6 and 262·6.

C₂₁H₁₆ requires C=93·97; H=6·03 per cent. M.W.=268.

The identity of this compound with Richter's was conclusively proved by analyses of its derivatives. On analysis of the bromo-derivative:

0·2389 gave 0·5185 CO₂ and 0·0763 H₂O. C=59·19; H=3·56.

0·2195 „ 0·1922 AgBr. Br=37·27.

C₂₁H₁₄Br₂ requires C=59·15; H=3·29; Br=37·55 per cent.

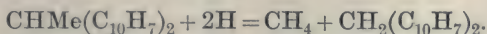
On analysis of the nitro-compound:

0·1505 gave 0·3083 CO₂ and 0·0438 H₂O. C=55·9; H=3·26.

0·1455 „ 14·92 c.c. N₂ (moist) at 11° and 748·4 mm. N=12·23.

C₂₁H₁₂(NO₂)₄ requires C=56·2; H=2·68; N=12·5 per cent.

The formation of ββ-dinaphthylmethane (C₂₁H₁₆) rather than of dinaphthylethane, C₂₂H₁₈, is probably explained by Bodroux's observation that methane and hydrogen chloride are evolved during the earlier stages of the condensation; possibly the latter hydrocarbon is first formed and subsequently converted into methane and ββ-dinaphthylmethane by the hydrogen evolved by the action of the aluminium chloride, thus:



It is scarcely probable that, as suggested by Bodroux, the fluorescent oil now shown to consist of dinaphthylmethane is a decomposition product resulting from distillation under diminished pressure; it is more probable that this hydrocarbon was not detected amongst the products of distillation under ordinary

pressure because of its decomposition at the high temperature necessary for its distillation.

Fraction iii (above $300^{\circ}/20$ mm.) was a deep red, viscous oil which deposited crystals. After purification these were obtained as a canary-yellow substance, melting at 252° , and giving an orange-coloured picrate. The quantity of this compound isolated was too small for analysis; it is possibly the s - $\beta\beta$ -dinaphthyl-ethane, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot C_{10}H_7$, melting at 253° , prepared by Bamberger and Lödter (*Ber.*, 1888, **21**, 55).

Thus the general result obtained is that the condensation products formed between *as*-dichloroethane and naphthalene, on distillation under *atmospheric pressure*, give the methylnaphthalenes and $\beta\beta$ -dinaphthyl, as stated by Bodroux; whilst, on distillation under *diminished pressure*, dinaphthylmethane and a small proportion of a substance melting at 252° are obtained, but practically no methylnaphthalenes or $\beta\beta$ -dinaphthyl.

(b) *Interaction of Methylene Chloride and Naphthalene.*

Bodroux (*loc. cit.*) was unable to isolate substances other than α - and β -methyl- and ethyl-naphthalenes and $\beta\beta$ -dinaphthyl.

In the present investigation the only crystalline substances obtained from the distillation of the products under diminished pressure were naphthalene and $\beta\beta$ -dinaphthyl, the latter identified by its melting point and the properties of its picrate. The failure to isolate dinaphthylmethane, $CH_2(C_{10}H_7)_2$, was probably due to the fact that the reaction had to be initiated at a temperature favourable to the preponderating effect of reaction (ii).

(c) *Interaction of Ethylene Bromide or Chloride and Naphthalene.*

Silva (*Bull. Soc. chim.*, 1881, [ii], **36**, 24) was unable to isolate substances other than α - and β -methyl- and ethyl-naphthalenes and $\beta\beta$ -dinaphthyl. Roux (*Ann. Chim. Phys.*, 1887, [vi], **12**, 297) obtained besides these substances a crystalline product melting at 300° , which he considered to be dinaphthyl-naphthalene, $C_{10}H_6(C_{10}H_7)_2$. Lespieau (*Bull. Soc. chim.*, 1891, [iii], **6**, 238) showed that Roux's hydrocarbon was identical with picene (m. p. 339°) obtained by Burg (*Ber.*, 1880, **13**, 1834) from the distillation of lignite tar.

In the present investigation it was found that the benzene extract of the products of the reaction, on cooling, deposited crystals, which, after purification, melted above 300° . The mother

liquors were then subjected to distillation *under diminished pressure* and two fractions isolated.

Fraction i (below 200°/10 mm.), on further distillation, gave small amounts of naphthalene and of an oil (230° and 280°). The latter gave a picrate melting at 139°, which is most probably the picrate of 1:4-dimethylnaphthalene (m. p. 139°).

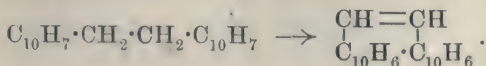
Fraction ii (above 250°/20 mm.) was an oil, depositing on cooling yellow crystals, which after several recrystallisations from benzene were ultimately obtained in white, glistening plates melting at 359°. The very slight solubility of the crystals, the green colour produced by concentrated sulphuric acid, and the fact that when mixed with a sample of picene kindly lent by Dr. Chattaway for spectroscopic purposes the melting point remained unchanged, showed the substance to be picene. Further, with the help of Mr. Purvis, definite proof of this identity was supplied by a study of the absorption spectra of the substance and a comparison of the results with those previously obtained in an examination of Dr. Chattaway's picene (Homer and Purvis, *loc. cit.*). The mean oscillation frequencies of the absorption bands were:

Dr. Chattaway's picene (<i>N</i> /1500-solution)	2662	2740	2790
Substance under consideration (<i>N</i> /1500-solution)	2670	2732	2784

No trace of $\beta\beta$ -dinaphthyl could be isolated from the products of the reaction.

These results confirm the work of Lespieau in so far as the substance formed is picene and not dinaphthylnaphthalene. But whilst Lespieau had great difficulty in separating the picene from $\beta\beta$ -dinaphthyl and methylnaphthalenes (the simultaneously-formed Lespieau's picene melted at 339°), in the present investigation no $\beta\beta$ -dinaphthyl was found, and in consequence the preparation of a very pure specimen of picene was an easy matter. Hence the Friedel-Crafts' reaction with ethylene bromide can be recommended as an easy method for the preparation of pure picene.

The production of picene instead of dinaphthylethane, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot C_{10}H_7$, must be due to a secondary reaction brought about either by a dehydrogenising effect of the aluminium chloride or by the action of heat on the dinaphthylethane first formed, thus:



(d) Interaction of Chloroform and Naphthalene.

Schwartz (*Ber.*, 1881, **14**, 1518) did not succeed in isolating any definite compound from the tarry product of the reaction. Hönig and Berger (*Monatsh.*, 1882, **3**, 668) obtained a crystalline substance melting at 189—190°, which they considered to be identical with synanthrene (m. p. 189—195°) isolated by Zeidler (*Annalen*, 1878, **191**, 298) from anthracene oil. Zeidler considered synanthrene to be identical with phosene, which had been shown by Barbier (*Compt. rend.*, 1874, **79**, 121) to be a mixture of anthracene and phenanthrene. Hönig and Berger further isolated two crystalline substances melting at 175° and 215° respectively.

The results obtained in the present investigation are as follows:

(B) *Distillation under reduced pressure* yielded three main fractions.

Fraction i (below 200°/20 mm.) gave on further distillation (a) naphthalene, (b) oils boiling between 220—230° and 230—240°, which were too small in amount to be further investigated, and (c) an oil which gave a portion (α) boiling between 248° and 252° and another (β) boiling between 260° and 270°.

Fraction (c) (α) still contained a little naphthalene which crystallised out on keeping. After the removal of the naphthalene, the residual oil began to deposit crystals when cooled to 0°. The crystals when freed from adhering oil gave a picrate which, when crystallised from benzene, melted at 115°, whereas when crystallised from alcohol it melted at 110°. Analyses of both specimens showed that this was the picrate of β-methylnaphthalene, which picrate is stated to melt at 115°. The oily filtrate, which remained liquid after being kept for some time in a freezing mixture, was proved by the analysis of its picrate (m. p. from alcohol 108°, Bodroux gives 116°) to consist of α-methylnaphthalene.

Fraction (c) (β) (between 260° and 270°) contained α-ethylnaphthalene, as shown by analysis of the picrate, which melted at 98—99°, a temperature identical with that given by Bodroux.

Fractions (ii) and (iii) were separately examined for the substance (m. p. 189—190°) obtained by Hönig and Berger. The distillates were extracted with light petroleum, alcohol, and benzene; but all these extracts yielded the same substance, which was recognised by its melting point and other properties as ββ-dinaphthyl. Determinations of the carbon and hydrogen are inadequate to corroborate this result and to supply conclusive proof that the main product of the reaction is ββ-dinaphthyl (C₂₀H₁₄), and not synanthrene (C₁₄H₁₀), as stated by Hönig and Berger:

C₂₀H₁₄ requires C = 94·49; H = 5·51 per cent. M.W. = 254.

C₁₄H₁₀ " C = 94·38; H = 5·62 " M.W. = 178.

Hönig and Berger, using Dumas's method, did not succeed in obtaining a trustworthy value for the molecular weight of their substance because of the decomposition occurring at the high temperature needed for volatilisation. The slight solubility of the substance makes the application of the cryoscopic methods of doubtful value; but the required proof is furnished by an analysis of a derivative such as the picrate (m. p. 182°):

0.2160 gave 22.42 c.c. N_2 (moist) at 19° and 751.8 mm. $N = 12.26$.

0.1878 „ 19.96 c.c. N_2 „ „ 19° „ 751.8 mm. $N = 12.34$.

$C_{20}H_{14}(C_6H_3O_7N_3)_2$ requires $N = 11.79$ per cent.

$C_{14}H_{10}(C_6H_3O_7N_3)$ „ $N = 10.07$ „

These figures prove conclusively that the compound isolated by Hönig and Berger, which they supposed to be identical with synanthrene, $C_{14}H_{10}$, was really $\beta\beta$ -dinaphthyl, $C_{20}H_{14}$.

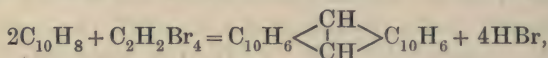
(A) *Distillation under the ordinary pressure* yielded products which, when carefully fractionated, gave methylnaphthalenes and $\beta\beta$ -dinaphthyl as under (B), and besides these a small amount of a crystalline substance melting at 210°, and probably identical with Hönig and Berger's fraction melting at 215°. The presence of this substance (m. p. 215°) would account for the fact that Hönig and Berger obtained a less pure sample of $\beta\beta$ -dinaphthyl than that obtained from the distillation under diminished pressure, in which no such fraction of higher melting point was present.

Thus the general result obtained shows that reactions (i) and (ii) occur simultaneously (p. 1141), and that whichever is the mode of separation and isolation, the products of the reaction are the same. The reaction proceeds so vigorously as to lead to considerable rise in temperature, which accounts (1) for the preponderating amount of $\beta\beta$ -dinaphthyl formed, (2) for the absence of trinaphthylmethane, $CH(C_{10}H_7)_3$, the primary product of the reaction, which by secondary reactions with the aluminium salt had been converted into the methyl- and ethyl-naphthalenes actually isolated. Friedel and Crafts have demonstrated the decomposing effect of aluminium chloride on complex hydrocarbons such as triphenylmethane at temperatures as low as 75° (Trans., 1882, **41**, 115).

Moreover, these results would lead one to expect that the action of carbon tetrachloride which has not been investigated is not likely to lead to the synthesis of tetranaphthylmethane.

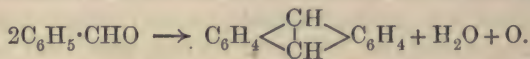
(e) *Interaction of Alkyl Tetrahalides and Naphthalene*, and (f) *Interaction of Nickel Carbonyl and Naphthalene*.

Lespieau (*loc. cit.*) and Hartenstein (*loc. cit.*) both tried to prepare a dinaphthanthracene by the action of *s*-tetrabromoethane on naphthalene, using the proportions required for the equation:



but in both cases the only crystalline product obtained was $\beta\beta$ -dinaphthyl. Hartenstein, however, succeeded in preparing a dinaphthanthracene by the following method: Concentrated sulphuric acid acting on 1:4-dihydroxynaphthalene-2-carboxylic acid produced by a process of oxidation and dehydration, followed by condensation, a quinone, $\text{C}_{22}\text{H}_{10}\text{O}_6$, which on distillation with zinc dust gave a hydrocarbon, $\text{C}_{22}\text{H}_{14}$, isomeric with picene (compare *Trans.*, 1908, **93**, 1319, where full details are given).

Dewar and Jones (*Trans.*, 1904, **85**, 212) had shown that nickel carbonyl, acting on hydrocarbons of the benzene series in presence of aluminium chloride, yields an aldehyde, which is subsequently reduced and condensed to an anthracene derivative, thus:



But when extending their investigations to naphthalene, they obtained as the main product of the reaction a crystalline substance, subsequently identified as $\beta\beta$ -dinaphthyl (Homer, *loc. cit.*). In addition to the $\beta\beta$ -dinaphthyl, they also isolated a small amount (0.03 gram) of an orange-coloured, crystalline substance, melting at 265° , which, however, they did not investigate.

The results obtained in the present investigation on the interaction of *s*-tetrabromo- or tetrachloro-ethane and naphthalene showed that the products of the reaction on distillation *under reduced pressure* yielded three fractions.

Fraction i (below $200^\circ/20$ mm.) and *Fraction ii* (between 200° and $280^\circ/20$ mm.) were not further investigated.

Fraction iii (above $300^\circ/20$ mm.) was a dark oil, which on cooling partly solidified to a mass of deep-coloured crystals. The crystals were repeatedly washed with light petroleum and cold benzene to free from adhering oil; they were then extracted with boiling alcohol to remove any $\beta\beta$ -dinaphthyl, and finally repeatedly crystallised from benzene, until a substance melting constantly at 267.5° was obtained. The serious difficulty encountered in the investigation of this substance was due to the extremely small amount available; although evidently formed in considerable quantity during the

reaction, the separation from the portions which could not be distilled was very cumbersome. Fractional extraction with xylene and other solvents was tried, but did not prove satisfactory. Distillation from a glass retort under the ordinary pressure yielded no better result as the substance was accompanied by a dark red, viscous oily product, which made the purification of the former a matter of great difficulty.

The substance thus obtained was insoluble in ether, alcohol, glacial acetic acid, or light petroleum; very sparingly soluble in cold benzene or xylene, hot alcohol, or hot glacial acetic acid; sparingly so in hot benzene, xylene, or ethylene bromide. When first prepared, it crystallised in lustrous plates of a deep orange colour, which persisted even after boiling the solutions with animal charcoal for several hours, or after distilling with animal charcoal, or after ten crystallisations from benzene and ethylene bromide. The purified substance readily sublimed in lustrous, orange plates, and gave fluorescent solutions.

With concentrated sulphuric acid at the ordinary temperature it gave a colour similar to that of an aqueous solution of potassium permanganate, and the liquid thus obtained, when considerably diluted, showed bands in the green region of the spectrum from $\lambda = 5500$ to $\lambda 5425$ (approx.) and from $\lambda 5300$ to $\lambda 5200$, whilst solutions twice as strong showed only one band, namely, $\lambda 5600$ to $\lambda 5200$. The addition of a drop of nitric acid to the sulphuric acid solution changed the colour to magenta; the magenta-coloured solution showed two bands at approximately $\lambda 5300$ to $\lambda 5200$ and $\lambda 4975$ to $\lambda 4825$, and in stronger solution only one band at $\lambda 5595$ to $\lambda 4670$.

On analysis of the orange crystals (m. p. 267.5°):

0.1650 gave 0.5703 CO_2 and 0.0812 H_2O . C = 94.26; H = 5.40.

0.0997 „ 0.3470 CO_2 „ 0.0465 H_2O . C = 94.9; H = 5.23.

$\text{C}_{22}\text{H}_{14}$ requires C = 94.96; H = 5.04 per cent.

As it is generally accepted that very close concordance cannot be obtained in analyses of hydrocarbons containing so high a percentage of carbon, and as the above results are, within the limits of experimental error, in good enough agreement with $\text{C}_{22}\text{H}_{14}$, the formula of the substance I had set out to prepare, it did not seem necessary to carry out further analyses at the cost of further quantities of the small amount of material at my disposal.

The very slight solubility of the hydrocarbon made it impossible to determine the molecular weight by cryoscopic methods. Of two determinations by Victor Meyer's vapour density method, using a lead bath, the one had to be discarded as worthless owing to decomposition of the substance; the other, carried out at a lower

temperature, gave the value 282 ($C_{22}H_{14}$ requires 278), which was considered as probably trustworthy, since inspection of the tube showed that there had been only very slight decomposition, and, as a matter of fact, the crystals were recovered and used again.

Analogy to anthracene would lead one to expect that if this hydrocarbon is an anthracene derivative, it would, on reduction with phosphorus and hydriodic acid, yield a hydride with the elimination of an anthracene cross-linking, and that this substance, as is the case with anthracene hydride, would be more soluble than the parent substance. If so, then the determination of the molecular weight of the hydride by cryoscopic methods would afford a check on the molecular weight of the parent substance, the value of which rests on the evidence of only one determination. The interaction of red phosphorus and hydriodic acid (D 1.7) with the hydrocarbon in sealed tubes at 250° gave a white, crystalline product, very soluble in acetone and benzene, and slightly soluble in alcohol, the white crystals melting constantly at 178.5° . On warming with sulphuric acid, the crystals gave a rose-pink colour, which in concentrated solution showed a band at (approximately) $\lambda=5800-5420$; addition of a drop of nitric acid to the sulphuric acid solution changed the colour to a beautiful red, which on warming gradually became rose-pink, and finally yellow. Treatment with picric acid in benzene solution gave an orange picrate. On analysis of the hydride:

0.0810 gave 0.2743 CO_2 and 0.0550 H_2O . $C=92.36$; $H=7.54$.

$C_{22}H_{20}$ requires $C=92.96$; $H=7.04$ per cent. M.W.=284.

$C_{22}H_{22}$ „ $C=92.39$; $H=7.69$ „ M.W.=286.

For compounds containing such a high percentage of carbon, the results of analyses alone cannot be relied on for furnishing sufficient evidence of deciding whether the hexa- or octa-hydride has been formed, although the results for the carbon and hydrogen are very near those required for the formula $C_{22}H_{22}$. However, the question as to which hydride has been formed does not materially affect the present investigation. An attempt to determine the vapour density of the hydride by Meyer's method (using a lead bath) failed owing to the decomposition of the substance. Molecular-weight determinations by the cryoscopic method, using benzene as solvent, gave 270 and 282, values which afford the required check for the molecular weight of the parent substance. They show that in the determination of the latter by a vapour density method, at the temperature of the experiment there had been no dissociation and no appreciable decomposition, and hence that the one value, namely, 282, can be regarded as trustworthy.

A picrate of the parent hydrocarbon was prepared. It con-

sisted of chocolate-coloured needles, and on recrystallisation from benzene melted constantly at 223—224°. Treatment of the hydrocarbon suspended in glacial acetic acid with chromic anhydride yielded an orange-yellow quinone sparingly soluble in boiling alcohol or benzene, and readily so in glacial acetic acid or pyridine; when purified by sublimation it melted at 335°.

The author next examined the crystals (m. p. 265°) obtained by Dewar and Jones from the nickel carbonyl reaction (p. 1148), and found that in appearance, colour, and solubility they were identical with the crystalline substance obtained in the interaction of tetrabromoethane and naphthalene just described. The identity of the two substances was conclusively proved by the following tests.

1. They both gave the same colour with concentrated sulphuric acid, the liquids exhibiting the same absorption bands.

2. In the mixed melting-point test no depression of the melting point took place.

3. The picrate of Dewar and Jones' compound was prepared; it consisted of chocolate-coloured needles (m. p. 223—224°), which did not lower the melting point (223—224°) of the picrate of the hydrocarbon $C_{22}H_{14}$.

It is thus evident that the five-ring compound which Dewar and Jones expected to obtain had, as a matter of fact, been formed, and was the orange-coloured, crystalline hydrocarbon which they had not investigated. The synthesis was repeated, using the aluminium salt and the naphthalene in the proportion of 1 : 5 instead of 1 : 1, as done by Dewar and Jones. No trace of naphthaldehyde could be found in the products of the reaction, whether allowed to proceed at the ordinary temperature or at 100°. From the crystalline product of the reaction there was obtained, besides $\beta\beta$ -dinaphthyl, which formed the bulk, a small amount of the crystalline hydrocarbon, melting at 267.5°. Although the distillation of the tarry residues was easy to control, yet the presence of so much $\beta\beta$ -dinaphthyl rendered the purification of the other substance so difficult a matter that the relative yield was not so good as that obtained under (e) when no $\beta\beta$ -dinaphthyl was formed.

The absence of naphthaldehyde in the products may be due to the fact that even at the ordinary temperature the aldehyde is acted on by the aluminium chloride as fast as it is formed. In order to test this hypothesis, an attempt was made to prepare naphthaldehyde by the Gatterman-Koch synthesis, but without success. It is thus evident that under the conditions of Dewar and Jones' experiment, naphthaldehyde cannot be obtained, and that nickel carbonyl acting on naphthalene yields besides $\beta\beta$ -di-

naphthyl, a small amount of a substance which can also be obtained by the Friedel-Crafts' synthesis with naphthalene and tetra-bromo- or -chloro-ethane.

The constitution of this hydrocarbon, melting at 267.5° , and obtained by the above two independent methods, is that of dinaphthanthracene, $C_{22}H_{14}$, for the following reasons:

I. (i) The formation of the substance by two distinct synthetical reactions, each of which in the benzene series yields anthracene derivatives, namely, (a) by Dewar and Jones' reaction, and (b) by the Friedel-Crafts' reaction with tetra-bromo- or -chloro-ethane, provides evidence of the strongest possible nature that the substance is a dinaphthanthracene compound.

(ii) The comparative study of the absorption spectra of the hydrocarbon under consideration, of its hydride, and of Hartenstein's compound, carried out in conjunction with Mr. Purvis, has shown that Hartenstein's compound and the $C_{22}H_{14}$ under consideration are isomeric dinaphthanthracenes.

II. The results of analyses (p. 1149) are in sufficiently good agreement with those required for $C_{22}H_{14}$, the preparation of which had been the main object of the research.

III. For a compound $C_{22}H_{14}$, the following structural formulæ are possible, if the formation of symmetrical six-carbon ring products only is assumed:



A. $\beta\beta\beta'\beta'$ -Dinaphthanthracene.



C. $\alpha\beta\alpha'\beta'$ -Dinaphthanthracene.



B. $\beta\beta\beta'\beta'$ -Dinaphthophenanthrene.



D. Picene.

of which, on the ground of the synthetical evidence given under I, A and C only need be considered; moreover, the melting point of the hydrocarbon, of its picrate, and of its quinone, together with the purple colour given with concentrated sulphuric acid, exclude the possibility of the formula D, which is that of picene. It remains therefore to decide between the formulæ A and C, and the evidence available clearly points to C.

(a) It has been previously stated that Hartenstein had prepared a dinaphthanthracene by the reduction of a quinone, $C_{22}H_{10}O_6$, with zinc dust. A comparison of the properties of the dinaphthanthracene compound synthesised from naphthalene and tetra-

chloroethane with those of Hartenstein's compound ($C_{22}H_{14}$) shows that the substances are different:

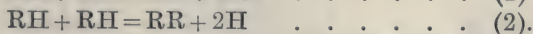
	Hartenstein's compound.	Compound synthesised from naphthalene and <i>s</i> -tetrachloroethane.
Melting point	About 260° , not sharp.	267.5° , sharp.
Appearance and colour.	White, lustrous plates, which readily sublime.	Yellow, lustrous plates, which readily sublime.
Colour with strong sulphuric acid.	On warming, <i>blue</i> . Strong solution shows an ill-defined band, λ 5800— λ 5600. Dilute solution shows very indistinct band.	In the cold, <i>purple</i> . Strong solution shows one band, λ 5600— λ 5200. Dilute solution shows two bands, λ 5500— λ 5425. λ 5300— λ 5200.
Quinone	M. p. $205-206^{\circ}$.	M. p. 335° .
Picrate		Chocolate-coloured needles, m. p. $223-224^{\circ}$.

The method of formation of Hartenstein's compound practically fixes the constitution as that of A, namely, $\beta\beta\beta'\beta'$ -dinaphthanthracene, since it is difficult to see how the condensation of 1:4-dihydroxynaphthalene-2-carboxylic acid could have taken place in any other way. The dinaphthanthracene (m. p. 267.5°) must therefore be the $\alpha\beta\alpha'\beta'$ -derivative. Conclusive direct evidence might have been obtained from the potash fusion of the quinone (m. p. 335°), which should have yielded α - and β -naphthoic acids, but unfortunately this could not be accomplished on account of the small amount of substance available.

(*b*) Further indirect confirmatory evidence is, however, furnished by a study of the other Friedel-Crafts' syntheses involving the use of naphthalene, which shows that in the cases where the reaction proceeds according to equation (i) (p. 1141) there is no preferential formation of α -derivatives at the expense of the β or vice versa; in the case of the action of dihalide alkyl derivatives on naphthalene, the substances isolated are either α - or β -mono-substitution products, or in cases where two hydrogens of the naphthalene molecules are eliminated, the compounds contain both α - and β -linkings, as is shown by the formation of picene from ethylene bromide.

Summary.

I. In Friedel-Crafts' syntheses with naphthalene and alkyl halides there is a simultaneous occurrence of two reactions:



In order that (1) may become effective, it is essential that (*a*)

the initial stage of the reaction should be allowed to proceed at the ordinary temperature, (b) the distillation of the products of the reaction should be carried out under diminished pressure.

II. (i) The action of *as*-dichloroethane under the above conditions yields β -dinaphthylmethane, formed as the result of a secondary reaction from dinaphthylethane.

(ii) In the case of methylene chloride, when it was not possible to work under these conditions, the only product was β 3-dinaphthyl.

(iii) The action of ethylene bromide yields picene as the result of a secondary action, namely, the decomposition of the *s*-dinaphthylethane, $C_2H_4(C_{10}H_7)_2$.

(iv) The action of chloroform does not yield synanthrene, as stated by Hönig and Berger, but $\beta\beta$ -dinaphthyl and monoalkyl-naphthalenes, due to a secondary reaction between aluminium chloride and trinaphthylmethane.

(v) The conditions have been described for the easy preparation of pure picene by means of the Friedel-Crafts' synthesis with ethylene bromide.

III. (i) From the products of the action of tetra-bromo- or chloro-ethane on naphthalene in presence of aluminium chloride there has been isolated a hydrocarbon, $C_{22}H_{14}$ (m. p. 267.5°), which on reduction gives a hydro-derivative melting at 178.5° .

(ii) The same hydrocarbon (m. p. 267.5°) has been isolated from the products of the action of nickel carbonyl on naphthalene in presence of aluminium chloride (Dewar and Jones' reaction).

(iii) The hydrocarbon isolated according to (i) and (ii) is not the same as Hartenstein's compound, $C_{22}H_{14}$ (m. p. $235-260^\circ$).

(iv) The chemical evidence supports the view that whilst Hartenstein's compound is a $\beta\beta\beta'\beta'$ -derivative, the hydrocarbon melting at 267.5° is an $\alpha\beta\alpha'\beta'$ -dinaphthanthracene.

In conclusion, the author wishes to thank Mr. H. O. Jones, M.A., of Clare College, Cambridge, for the keen interest taken in the progress of the work described in this paper.

The expenses of the research were in part defrayed by a grant from the Research Fund of the Chemical Society.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

XCVII.—*The Absorption Spectra of Dinaphthanthracene and its Hydro-derivative Compared with the Absorption Spectra of its Isomerides.*

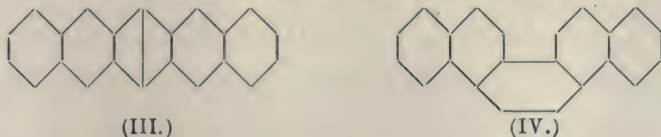
By ANNIE HOMER and JOHN EDWARD PURVIS.

A SPECTROSCOPIC examination of the hydrocarbon, $C_{22}H_{14}$, melting at 267.5° , considered to be $\alpha\beta\alpha'\beta'$ -dinaphthanthracene (I), together



with its hydride melting at 178.5° (II), which may be either the hexahydride, $C_{22}H_{20}$, or the octahydride, $C_{22}H_{22}$, described in the preceding paper, should furnish additional evidence as to the presence of an anthracene linking in the parent substance. The destruction of an anthracene cross-linking caused by the reduction of the hydrocarbon, $C_{22}H_{14}$, to a hexa- or octa-hydro-compound should be evidenced by some distinctive differences in the absorption spectra.

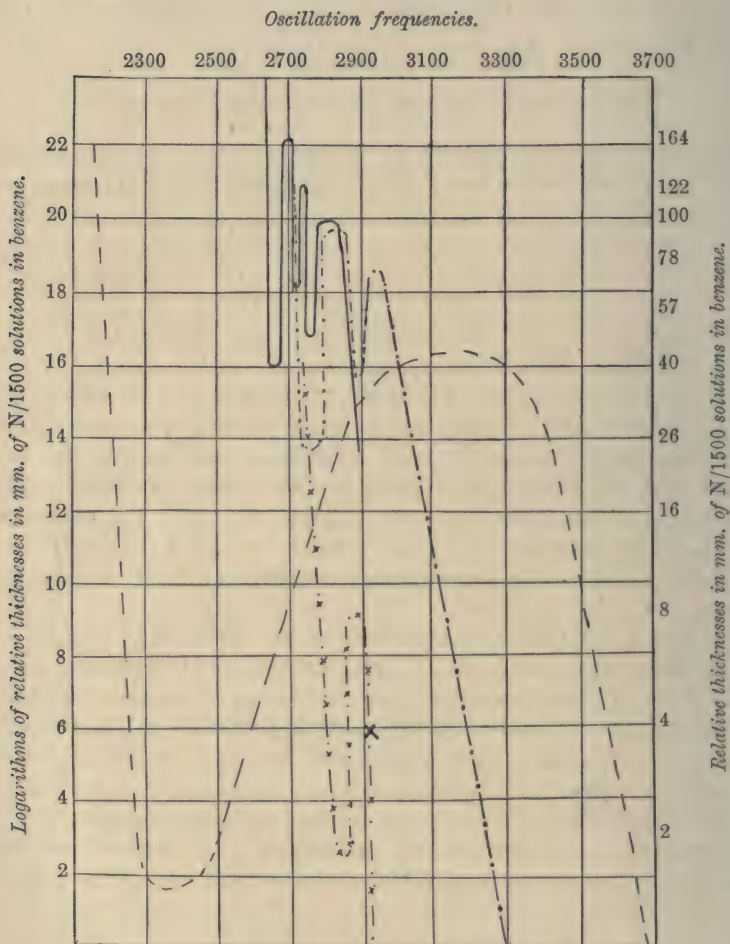
At the same time a comparison of the absorption spectra of Hartenstein's compound, which, from its method of formation, must have the $\beta\beta\beta'\beta'$ -configuration, and of the $\alpha\beta\alpha'\beta'$ -dinaphthanthracene (m. p. 267.5°) and of its hydride (m. p. 178.5°) might indicate whether his substance is a dinaphthanthracene, or, as has been suggested, a dihydrodinaphthanthracene, presumably a derivative in which the anthracene cross-linking no longer exists. The configuration of Hartenstein's compound, if a dinaphthanthracene, would be expressed by (III). Further, the absorption curves



of these substances were also compared with those of picene, for the latter substance is characterised by the absence of an anthracene linking, its constitutional formula being represented by (IV).

The experimental conditions of the investigation were the same as those employed in the investigation of the absorption spectra of

picene, tetramethylpicene, and Hartenstein's compound (Homer and Purvis, *Trans.*, 1908, **93**, 1319). Solutions in benzene of *N*/1500-strength of the hydrocarbons were used. The resulting absorption



Full curve : $N/1500$ -solution of picene in benzene.
 Dash curve : $N/1500$ -solution of $C_{22}H_{14}$ (*m. p.* 267.5°) in benzene.
 Dot and dash curve : $N/1500$ -solution of $C_{22}H_{20}$ in benzene.
 Dot, cross, and dash curve : $N/1500$ -solution of Hartenstein's $C_{22}H_{14}$ in benzene.

spectra have been plotted in the accompanying curves, so that the abscissæ represent the oscillation frequencies, and the ordinates the logarithms of the relative thicknesses of the solutions.

It will be noticed that the supposed $\alpha\beta\alpha'\beta'$ -dinaphthanthracene

exhibits one large persistent band, which commences about 2360 (oscillation frequency). The absorption band at all thicknesses includes that portion of the visible spectrum commencing between the green and blue solar lines F and G, and this accounts for the persistent yellow colour of the hydrocarbon. Solutions of the hydrocarbon have a green fluorescence.

The hydride of $C_{22}H_{14}$ has a different type of curve from that of the parent substance. It is characterised by two bands in the ultra-violet region of the spectrum, which commence about 2760 and 2880 (oscillation frequencies).

These results strengthen the supposition that the process of reduction has produced some fundamental change, such as the suggested elimination of an anthracene cross-linking, for the mere addition of six or eight hydrogen atoms to the molecule could hardly cause so complete a change in the character of the curve. The types of the two absorption curves of the reduced compound are not unlike two of those of picene where the anthracene linking is absent, whilst the angular linking or space configuration is possibly the origin of the two bands as compared with the three bands of picene where the linking of the rings is more symmetrical.

That Hartenstein's compound contains an anthracene linking is indicated by the fact that the absorption curve is marked by one persistent band, such as is shown by $\alpha\beta\alpha'\beta'$ -dinaphthanthracene, and not by the two or three bands, which are the features of the hydro-dinaphthanthracene and picene curves respectively.

It is interesting to notice that the position and persistency of the band exhibited by the curves for the isomeric dinaphthanthracenes differ so markedly. The band of the coloured $\alpha\beta\alpha'\beta'$ -compound is much more persistent and nearer the red end of the spectrum than that of Hartenstein's colourless compound. It seems as though the space configuration, or, to express it another way, the angular linking of the dinaphthanthracene, is such that the vibrations of the atoms within the molecule have a greater amplitude than those in the molecule of the isomeric compound of Hartenstein's. The latter compound is marked by a linear linking of the rings, whilst the former is more angular.

These results strengthen the supposition that Hartenstein's compound and the hydrocarbon formed by the action of *s*-tetrabromoethane on naphthalene in the presence of aluminium chloride are isomeric dinaphthanthracenes.

It is also of considerable importance to note that the isomeric dinaphthanthracenes show one absorption band, that the hydro-derivative of the $\alpha\beta\alpha'\beta'$ -compound shows two bands, and that picene shows three bands. The two bands of the hydride of $C_{22}H_{14}$

probably correspond with the two less refrangible bands of picene. The bands of picene are nearer the red end of the spectrum than the corresponding bands of the hydride, and they are also much more persistent. The origin of these differences may be sought for in differences in the space configurations or the angular linkings of the rings of the two compounds. The linkings of the rings of picene are symmetrically arranged as compared with those of the hydrodinaphthanthracene compound.

Results.

The results of the preceding investigation are that:

1. The spectroscopic evidence supports the proposition that the hydrocarbon $C_{22}H_{14}$, melting at 267.5° , is a dinaphthanthracene compound, and that its hydride, $C_{22}H_{20}$, no longer contains an anthracene linking.

2. Hartenstein's substance is not a dihydrodinaphthanthracene, but a dinaphthanthracene isomeric with the dinaphthanthracene compound, melting at 267.5° , and with picene. The absorption curves indicate similarity in the type of configuration of Hartenstein's compound and the $C_{22}H_{14}$, melting at 267.5° , which differs markedly from that of the isomeric picene.

3. The origin of the differences in the absorption bands of the above four compounds may be explained by a consideration of differences in the anthracene linkings and in the angular or linear linkings of the rings.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

XCVIII.—*Ionic Equilibrium in Solutions of Electrolytes.*

By JAMES RIDDICK PARTINGTON.

THE Dilution Law of Ostwald (*Zeitsch. physikal. Chem.*, 1888, **2**, 36) may be deduced by an extension of the law of chemical mass-action (which has been theoretically and experimentally verified for the case of the thermal dissociation of a gas), to the equilibrium which is assumed to exist between the molecules of a salt in dilute solution, and the ions of the salt. It is assumed that on passing into solution the salt molecules have to a greater or less degree disappeared, and their place has been taken by electrically charged

portions of the molecules, called ions. The fraction of the total amount of salt which is ionised in this way is defined as the degree of ionisation, α . The thermodynamic deduction of the mass-law then proceeds on the same lines as the investigation of gaseous equilibrium. The methods of proof used by different authors (van't Hoff, Nernst, Planck) are at first sight somewhat different; an examination of the assumptions entering into each system shows, however, that all are either directly, or (by means of theorems on entropy or thermodynamic potential) indirectly, based on the fundamental assumption that it is legitimate to consider the ions and non-ionised salt separated isothermally and reversibly from the solution at the concentrations existing in the equilibrium state. It is sufficient, for this purpose, to show that there exist actual diaphragms having a selective permeability, doubtless imperfect, for ions; and the extension to perfect membranes is then legitimate, provided that reversible effects at the surfaces, or in the interior, of the membranes have not been overlooked. A thin plate of iron is known to be permeable to hydrogen ions at the ordinary temperature, and the membranes of plant structures are very frequently selectively permeable to ions. The postulation of ideal membranes as a limiting case is therefore legitimate. If the salt is added to the solution in an equilibrium box through one membrane, and the ions withdrawn through two others so that the composition of the solution remains unchanged, the process is reversible. It is true that the contents of the cylinders containing the ions acquire electrical charges, and if the cylinders are placed opposite to each other the system constitutes a condenser, to charge which additional work must be done. But by separation of the cylinders this work can be made vanishingly small in comparison with the osmotic work, which is independent of the form or size of the apparatus, and thus the work of electrical separation vanishes in the limit.

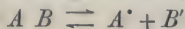
The thermodynamic investigations lead to the equilibrium isotherm:

$$n' \log c' + n'' \log c'' + n''' \log c''' + \dots = \log K,$$

where K is a function of the temperature and total pressure for given components, but is constant at constant temperature and pressure. K is independent of the molecular concentrations (c) and numbers of molecular weights (n) of the components. Thus:

$$c'^{n'} \cdot c''^{n''} \cdot c'''^{n'''} \dots = K \dots \dots \dots (1).$$

For the ionisation of a binary electrolyte:



$$(c_0) \quad (c_1) \quad (c_2)$$

$$c_0/c_1^2 = K \dots \dots \dots (2),$$

since $c_1 = c_2$.

If n_0, n_1, n_2 are the corresponding numbers of molecular weights of the components,

$$c_0 = n_0 / (n_0 + 2n_1 + n),$$

$$c_1 = c_2 = n_1 / (n_0 + 2n_1 + n),$$

where n refers to the solvent.

If n_0, n_1 are small compared with n ,

$$n_0 n / n_1^2 = \text{constant}.$$

Let v be the volume of solution containing one molecular weight of total salt, then

$$n = kv(n_0 + n_1),$$

where k is a constant of proportionality.

Thus finally,

$$\frac{n_0}{n_1^2} (n_0 + n_1) v = \text{constant} \quad . \quad . \quad . \quad (3).$$

This equation is as far as thermodynamic theory will proceed; to bring the result into a region accessible to experimental test, a further assumption is necessary. The determination of n_1 , the ionic concentration, is made possible if we accept Arrhenius's fundamental theorem that the ratio of the number of "active" (or ionised) molecules of the electrolyte to the total number, active and inactive, present in a given portion of solution is equal to the ratio of the molecular electrical conductivity of the solution to the limiting value of this when the dilution is very great:

$$n_1 / (n_0 + n_1) = \Lambda / \Lambda_\infty = a \quad . \quad . \quad . \quad (4).$$

Substituting in (3) the value of $n_1 / (n_0 + n_1)$ from (4):

$$\frac{(\Lambda / \Lambda_\infty)^2}{(\Lambda - \Lambda_\infty) v} = \text{constant} = K \quad . \quad . \quad . \quad (5).$$

This is Ostwald's Dilution Law.

The thermodynamic derivation shows that the formula can, in any case, represent the course of ionisation only in solutions of such dilution that the regions of solvent influenced by each molecule of solute are independent. Any further addition of pure solvent then serves merely to separate these regions to greater distances, and thus all considerations as to the mode of influence of the solute on the solvent, such as the extent or manner of hydration of the solute, are not germane to the problem (compare Larmor, "Æther and Matter," Cambridge, 1900, page 286). The present discussion is confined entirely to solutions which may be regarded as approximating to this limiting case; a sharp distinction must be drawn between such dilute solutions of "strong" (that is, largely ionised) electrolytes and strong solutions (that is, solu-

tions in which n is not very large in comparison with n_0 and n_1). The disturbing influences introduced by increasing concentration, and by increasing ionisation, may act in opposite directions, and the observed results may be affected by both factors (Wegscheider, *Zeitsch. physikal. Chem.*, 1909, **69**, 603).

Experimental investigation of the conductivities of dilute solutions led to the result that Ostwald's equation was satisfactorily applicable to the cases of weak organic acids (W. Ostwald, *Zeitsch. physikal. Chem.*, 1899, **3**, 170, 241, 369) and weak organic bases (G. Bredig, *ibid.*, 1894, **13**, 289; Goldschmidt and Salcher, *ibid.*, 1899, **29**, 89); strong acids and bases, and their salts, gave results widely divergent from the theory.

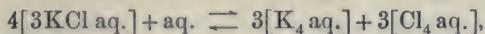
Empirical formulæ were proposed by Rudolphi (*Zeitsch. physikal. Chem.*, 1895, **17**, 385) and van't Hoff (*ibid.*, 1895, **18**, 300). The latter wrote:

$$c_1^3/c_0^2 = \text{constant} \quad . \quad . \quad . \quad . \quad . \quad (6).$$

F. Kohlrausch (*ibid.*, 1895, **18**, 662) pointed out that van't Hoff's equation amounts to the statement:

$$c_1/c_0 = \text{constant} \times \text{mean distance between non-ionised molecules.}$$

W. Vaubel (*Zeitsch. angew. Chem.*, 1902, 395) attempted to deduce van't Hoff's equation on the assumption of ionic hydration and a polymerisation of water to $(\text{H}_2\text{O})_6$. W. R. Bousfield (*Zeitsch. physikal. Chem.*, 1905, **53**, 266; *Proc. Roy. Soc.*, 1905, **74**, 563; *Phil. Trans.*, 1906, **206**, 101, 155) also deduced the equation by assuming that the salt and its ions are polymerised and hydrated. If the equation of ionisation of potassium chloride is written:



the equilibrium isotherm leads to van't Hoff's equation. This method will obviously serve to "deduce" any other equation desired; it is merely requisite to choose the proper coefficients in the chemical equation.

L. Storch (*Zeitsch. physikal. Chem.*, 1896, **19**, 13; 1900, **26**, 545) and W. D. Bancroft (*ibid.*, 1899, **31**, 188; compare F. Kohlrausch, *ibid.*, 1895, **18**, 662; *Beibl. Ann. Physik.*, 1901, **25**, 54), observing that Ostwald's and van't Hoff's formulæ represented two limiting conditions, proposed to cover all intermediate cases by the formula:

$$c_1^n/c_0 = \text{constant} = K^1, \quad . \quad . \quad . \quad . \quad . \quad (7),$$

in which n and K^1 are functions of the chemical composition of the electrolyte, but are constants for a particular electrolyte under the same restrictions as apply to Ostwald's formula. The course of

ionisation is thus represented by a purely empirical interpolation formula, comparable with those of Biot and Magnus for the dependence of the vapour pressure of a liquid on the temperature.

The literature containing attempts at a theoretical explanation of the divergencies of strong electrolytes from the law of mass-action is very voluminous, but it would appear that most of the explanations can be placed in one or other of five groups. These will be briefly considered.

(1) *The errors incident to the measurements are large enough to produce the observed deviations.*

Ostwald (*Grundr. Allgem. Chem.*, 1899, 406) pointed out that in the case of strong electrolytes, $(1-\alpha)$ is small, and a small error committed in the determination of α would produce a considerable change of K :

$$\frac{\delta K}{\delta \alpha} = \frac{2\alpha - \alpha^2}{v(1-\alpha)^2}.$$

The possible constant errors, due to impurities in the solvent water, or dissolved from the glass cell, or from salt adsorbed on the electrodes, would increase in their influence on the magnitude of K as the dilution was increased, and would act in the direction of an abnormally large value of α . V. Rothmund and K. Drucker (*Zeitsch. physikal. Chem.*, 1903, **46**, 827; K. Drucker, *ibid.*, 1904, **49**, 563) conclude that the limiting values of the conductivities at great dilution are not known with sufficient accuracy to give concordant values of K . It is of interest to notice that according to Völlmer (*Wied. Ann.*, 1894, **52**, 328) deviations are exhibited by potassium and sodium iodides dissolved in methyl or ethyl alcohol, although these salts are perceptibly less dissociated in these solvents than in water, and the results are therefore less sensitive to errors in the determination of α . Drucker (*loc. cit.*; also *Die Anomalie der stärken Elektrolyte*, Ahrens' Sammlung, 1905, **12**) finds that if slightly different values of the limiting conductivities are taken, the results are improved, and it is not impossible that part of the discrepancies may be due to the cause considered in this section.

(2) *The method of calculating the degree of ionisation is inaccurate.*

It has been pointed out (F. Kohlrausch, *Wied. Ann.*, 1893, **50**, 388; H. Jahn, *Zeitsch. physikal. Chem.*, 1898, **27**, 358; 1900, **33**, 545; **35**, 8; 1901, **37**, 679; 1907, **58**, 641; compare Noyes and Kato, *Reports Carnegie Inst., Washington*, 1907, 326; Drucker and Kršnjavi, *Zeitsch. physikal. Chem.*, 1908, **62**, 742; Sackur, *Zeitsch. Elektrochem.*, 1901, **7**, 784; Goodwin and Haskell, *Zeitsch. physikal. Chem.*, 1905, **52**, 630; Löb and Nernst, *ibid.*, 1888, **2**, 956; Bein, *ibid.*, 1898, **27**, 49) that Arrhenius's formula, $\alpha = \Lambda/\Lambda_{\infty}$, can, in

any case, be exact only when the ionic mobilities u and v are not functions of the concentration. For:

$$\Lambda = \alpha(u + v),$$

$$\Lambda_{\infty} = u_{\infty} + v_{\infty},$$

$$\therefore \alpha = \Lambda / \Lambda_{\infty} \text{ only if the condition}$$

$$u + v = u_{\infty} + v_{\infty}$$

is satisfied. In strong solutions this is certainly not the case, but the experimental evidence available seems to indicate that the mobilities approach limiting values at great dilution, and may then be taken as constant over a moderate range (compare A. A. Noyes, *Tech. Quart.*, 1904, **17**, 295; S. Arrhenius, *Zeitsch. physikal. Chem.*, 1901, **37**, 316). The views on this fundamental question are, however, conflicting. Jahn concludes that Arrhenius's formula is applicable to weak electrolytes only, and must be abandoned in the case of strong electrolytes at moderate dilutions. It must also be remembered that the values of α derived from the freezing-point measurements agree with those given by the conductivities within the somewhat large limits of experimental error (Abegg, *Zeitsch. physikal. Chem.*, 1889, **3**, 198; Jahn, *ibid.*, 1894, **15**, 339; 1896, **19**, 233; compare Whetham, *Phil. Trans.*, 1900, A, **194**, 321). The values of K calculated from freezing-point measurements also increase with increasing concentration (Loomis, *Wied. Ann.*, 1894, **51**, 500; 1896, **57**, 495), so that the discrepancies seem to depend on some physical cause inherent in the process of ionisation itself. Drucker, however (*Anomalie, loc. cit.*), thinks that no certain calculation of the degree of ionisation can be made from the freezing point, and the differences between the values of α obtained by different methods do not exclude the explanation of part of the divergencies by the indefinite character of the degree of ionisation determined by the conductivity method (compare Abegg, *Theorie der elektrolytische Dissociation*, Ahrens' Sammlung, 1903, p. 232).

(3) *The discrepancies are due to the formation of complex ions, the mass-law being assumed to be correct.*

The reaction occurring when the salt is dissolved is assumed, on this hypothesis, to be more complicated than a separation of the molecule into its positive and negative radicles; a part, or the whole, of the simple ions may combine with the solvent to form hydrated ions, or may combine with a part of the non-ionised salt to form complex ions. This may take place after simple ionisation, or, as would seem more probable, may be a necessary condition for ionisation to occur at all. The possibility of the formation of hydrated ions does not affect the matter at all, since only dilute solutions (that is, solutions in which the active mass of the water

is constant) are contemplated, and in this case ionic hydration leads to the same equations as the simpler hypothesis, the only difference being that the total conductivity is now made up of a sum of terms representing the mobilities of the different ionic hydrates (compare Morgan and Kanolt, *Zeitsch. physikal. Chem.*, 1904, **48**, 366; R. Wegscheider, *ibid.*, 1909, **69**, 603, 609; W. Nernst, *Theoretische Chemie*, 1907, p. 464). The same conclusion was reached at an earlier stage of the present discussion from the more general considerations of molecular theory. The formation of complex ions, however, renders Ostwald's formula invalid, and leads, under qualified assumptions, to an approximation to van't Hoff's formula (compare Morgan and Kanolt, *loc. cit.*; Bousfield, *loc. cit.*). Direct evidence for the existence of such complex ions has been available since the time of Hittorf's pioneering work, and additions have been made by other more recent observers (Abegg and Labendzinski, *Zeitsch. Elektrochem.*, 1904, **10**, 77; Abegg, *Theorie der elektrolytische Dissociation*, 230; Biltz, *Zeitsch. physikal. Chem.*, 1902, **40**, 221; Bruni, Pellini, and Pegoraro, *Zeitsch. Elektrochem.*, 1907, **13**, 621). There is no evidence for the presence of complex ions in solutions of such salts as potassium chloride, which show deviations from Ostwald's formula, and this method of explanation cannot be regarded as sufficient.

(4) *The theory of a partial dissociation into ions is inaccurate.*

W. Sutherland in a series of papers (*Phil. Mag.*, 1902, [vi], **3**, 161; 1905, **11**, 781; 1906, **12**, 1; 1907, **14**, 1; 1908, **16**, 497; compare F. Barmwater, *Zeitsch. physikal. Chem.*, 1899, **28**, 130) has put forward the hypothesis that the ionisation of all ordinary electrolytes in solutions of all concentrations is complete. The differences of molecular conductivity at different dilutions are assumed to be due to the action of the ordinary viscosity of the solution and to two new types of viscosity of electric origin. He believes that "the theory of solution will have to be re-written." Until this has been done, it is impossible to say how much of the data correlated by the present ionic theory will agree with the theory of Sutherland.

(5) *The law of mass-action is not applicable to ionisation.*

Arrhenius seems to have been the first to suggest that the fundamental law of mass-action may not hold good in the case of strong electrolytes, and consequently the dilution law of Ostwald, being based on the law of mass-action, will give incorrect results. He suggested that K in the equation $c_1^2 = Kc_0$ is not a constant, but rather a function of the total ion concentration (*Zeitsch. physikal. Chem.*, 1899, **31**, 197; 1901, **36**, 28; 1901, **37**, 490; compare Noyes and Abbot, *ibid.*, 1895, **16**, 125; J. J. van Laar, *ibid.*, 1909, **69**, 433). The ions have the effect of stimulating the dissociation of the

salt, or increasing the ionising power of the solvent. This "salt-action" of the ions, analogous to, and probably identical with, the influence of the ions of neutral salts on the catalytic activity of weak acids, is a maximum for a salt, and it is greater in the case of acids the more strongly ionised is the acid. According to Arrhenius, Ostwald's dilution law is not strictly correct for any actual substance, but in the case of weakly dissociated acids and bases the error, owing to the small concentration of the ions, falls within the limits of experimental error. Thus, Arrhenius's theory amounts to writing:

$$c_1^2/c_0 = f(c_1) \dots \dots \dots (8),$$

instead of $c_1^2/c_0 = \text{constant}$.

Noyes (*Tech. Quart.*, 1904, **17**, 298) also concludes that the degree of ionisation of salts, whether derived from conductivity or freezing-point measurements, does not vary with the concentration even approximately in accordance with the law of mass-action. He therefore rejects the theoretical basis, and makes use of the purely empirical formula proposed by Barmwater (*Zeitsch. physikal. Chem.*, 1899, **28**, 130; 1903, **45**, 557; 1906, **56**, 225):

$$1 - \alpha = k(c\alpha)^{\frac{1}{2}} \dots \dots \dots (9).$$

The degree of ionisation is assumed to be accurately calculable by means of the equation $\alpha = \Lambda/\Lambda_\infty$, because the electromotive forces of concentration cells, calculated on the assumption that α changed with concentration in accordance with the empirical equation, agreed to 1 per cent. in the case of potassium and sodium chlorides between the concentrations of $N/600$ and $N/20$. The case against the law of mass-action Noyes regards as strengthened by the result that the empirical formula gave equally good results with salts dissociating into two, three, or four ions, the concentration of non-ionised salt being in all cases proportional to the $3/2$ power of the ion concentration.

G. N. Lewis, in a thermodynamic study (*Proc. Amer. Acad.*, 1907, **43**, 287), also concludes that the mass-law requires modification in the case of strong electrolytes, but makes no suggestion as to the quantitative formulation.

The most comprehensive treatment of the equilibrium of a strong electrolyte with its ions from this point of view is contained in a series of papers by Jahn (*Zeitsch. physikal. Chem.*, 1900, **33**, 545; 1900, **35**, 1; 1901, **36**, 453; 1901, **37**, 490; 1902, **41**, 257) and by Nernst (*ibid.*, 1901, **38**, 125, 457; compare P. Henderson, *ibid.*, 1907, **59**, 1). Both authors deal with dilute solutions, and arrive at modified formulæ by thermodynamic methods, the modifications required in the ordinary assumptions having been previously pointed out by Planck (*Thermodynamics*, Eng. trans. by Ogg, 1903,

225, 234). Instead of setting the total energy and total volume of the solution equal to the sums of the energies and volumes of the components, as in the ordinary derivation of the mass-law, terms are introduced to allow for the mutual interactions of the different molecular species. By rather different methods, the two authors then arrive at modified equations:

$$(I.) \quad \frac{n_1^2}{N-n_1} e^{-\frac{aN}{n} + n_1 \left(\frac{2a}{n} - \frac{b}{n} \right)} = \text{constant (Jahn)}. \quad (10),$$

where N = total salt concentration,

n_1 = ion concentration,

e = base of the natural logarithms,

a, b, K = constants.

$$(II.) \quad \frac{c_1^2}{c_0} e^{2c_1(\mu_1 + \mu_{12} - \mu_{01}) + c_0(2\mu_{01} - \mu_0)} = \text{constant (Nernst)} \quad (11),$$

where c_1, c_0 = concentrations of ions and salt,

e = base of the natural logarithms,

μ_1, μ_0 = coefficients of influence between ions and between neutral molecules,

μ_{01} = coefficient of influence between molecules and ions,

μ_{12} = coefficient of influence between the two kinds of ions.

This differs from Jahn's equation in taking account of the action between neutral salt molecules. The coefficients are determined by trial (J. B. Goebel, *Zeitsch. physikal. Chem.*, 1902, **42**, 59; F. Hoffmann and K. Langbeck, *ibid.*, **51**, 384; P. Henderson, *ibid.*, 1907, **59**, 124; B. von Szyszkowski, *ibid.*, 1907, **58**, 420; 1908, **63**, 421; V. Rothmund, *ibid.*, 1909, **69**, 523).

The methods used in deducing the two formulæ are still rather empirical, amounting really to an expansion of U, V (total energy and volume) into series, these quantities being regarded as finite, continuous, and differentiable functions of several variables. In the simple case, when these variables are small, the functions are necessarily linear, and Ostwald's equation is the result. To obtain a physical representation of the relations, one may revert to the idea of Arrhenius. Larmor (Wilde Lecture, *Mem. Manchester Phil. Soc.*, 1908, **52**, 33, 53) has considered the action of the ions on the ionisation of an electrolyte from another and, it appears to the author, different point of view. The rapidly moving ions produced in gases subjected to the action of Röntgen rays, or the rays from radioactive substances, by their collision with neutral gas molecules lying in their path, facilitate the ionisation of the latter in a marked degree (J. S. Townsend, *Phil. Mag.*, 1901, [vi], **1**, 198, 630; 1903, **6**, 598). Larmor suggested that a similar influence

may be exerted by the ions in an electrolytic solution. Assuming this ionising influence to be proportional to the number of collisions in unit time between ions and molecules, the total rate of ionisation will be:

$$\frac{dc_1}{dt} = kc_0 + k'c_0c_1,$$

and that of ionic recombination:

$$\frac{dc_1}{dt} = -k''c_1^2,$$

k, k', k'' being constants.

For equilibrium, therefore,

$$kc_0 + k'c_0c_1 = k''c_1^2,$$

or

$$c_1^2/(1 + \rho c_1) = \chi c_0, \quad . \quad . \quad . \quad (12),$$

where $\rho = k'/k$, $\chi = k/k''$ are constants for a particular electrolyte and solvent at a given temperature. Larmor did not test the equation by any actual example.

It appears that the influence of the ions, instead of being purely statical, and consisting of attractive and repulsive forces, is dynamical, being more concerned in the production of ions from molecules than in the condition of the system after such ionisation has occurred. The actual mechanism of ionisation is still far from clear, even in the case of gases, but it is interesting to notice that only solvents which are themselves electrical conductors, and therefore contain some free ions, are good ionising media. The presence of ready-formed ions may, especially in view of what has just been said, be a necessary condition for the ionisation of a dissolved salt.

The experimental verification of the effect of the ions in an electrolyte might be attempted by examining the effect of a strong transverse magnetic field on the conductivity of a solution. If the lines of current flow were made parallel by using large electrodes in the form of parallel plates, the Hall effect would produce no change in the conductivity; and if any such change were observed, it would render very probable the ionising effect of moving ions which forms the basis of the present discussion.

The author has tested Larmor's equation by substituting the values of the ionic concentration derived from conductivity measurements, using the results of three observers who employed different methods. "K" denotes F. Kohlrausch (*Wied. Ann.*, 1885, **26**, 195; Kohlrausch and Holborn, *Leitvermögen der Elektrolyte*), "V" denotes Vincentini (*Atti R. Accad. Sci. Torino*, 1885, **20**, 688), "F" denotes Fitzpatrick (*Phil. Mag.*, 1887, [v], **24**, 377).

The equation is easily modified to:

$$a^2/(1-a)(v + \rho a) = \chi, \quad . \quad . \quad . \quad (13),$$

which is the most convenient form.

Values of ρ and χ were found by substituting the first and last values of α and v given in the portion of the tables used, intermediate values were then taken, and χ calculated for each. For purposes of comparison, the "constant" K calculated by Ostwald's formula is given.

If α is small and ρ small, the equation reduces to Ostwald's form,

$$\alpha^2/(1-\alpha)v = \chi$$

which may be regarded as a special case.

(1) *Potassium chloride* (V). $\Lambda_{\infty} = 130.31$. $\rho 26 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
1031×10^3	125.4	0.9624	1.91×10^{-5}	2.39×10^{-5}
515×10^3	121.1	0.9293	1.61×10^{-5}	2.35×10^{-5}
257×10^3	118.0	0.9055	1.76×10^{-5}	3.37×10^{-5}
100×10^3	114.8	0.8794	1.95×10^{-5}	6.52×10^{-5}
54×10^3	112.7	0.8633	1.91×10^{-5}	10.25×10^{-5}

(2) *Lithium chloride* (F). $\Lambda_{\infty} = 98.84$. $\rho 18 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
513×10^3	95.4	0.9652	3.9×10^{-5}	5.2×10^{-5}
256×10^3	93.8	0.9490	4.0×10^{-5}	6.9×10^{-5}
128×10^3	92.9	0.9399	4.8×10^{-5}	11.5×10^{-5}
64×10^3	90.2	0.9126	3.9×10^{-5}	14.9×10^{-5}

(3) *Sodium chloride* (K). $\Lambda_{\infty} = 109$. $\rho 27 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
1667×10^3	107.7	0.9792	2.4×10^{-5}	2.7×10^{-5}
1000×10^3	107.1	0.9737	3.1×10^{-5}	3.6×10^{-5}
500×10^3	106.1	0.9624	3.2×10^{-5}	4.9×10^{-5}
167×10^3	103.7	0.9428	3.6×10^{-5}	9.3×10^{-5}
100×10^3	102.3	0.9301	3.5×10^{-5}	12.3×10^{-5}
33×10^3	98.7	0.8974	2.8×10^{-5}	23.7×10^{-5}
20×10^3	95.3	0.8664	2.4×10^{-5}	23.0×10^{-5}

(4) *Ammonium chloride* (K). $\Lambda_{\infty} = 129.8$. $\rho 17.5 \times 10^5$.

v c.c.	Λ .	α .	χ .	K .
107	128.5	0.9897	0.81×10^{-5}	0.95×10^{-5}
5×10^6	128.0	0.9858	0.96×10^{-5}	1.3×10^{-5}
167×10^4	127.3	0.9804	1.4×10^{-5}	2.9×10^{-5}
10^6	126.5	0.9743	1.3×10^{-5}	3.7×10^{-5}
5×10^5	125.5	0.9666	1.2×10^{-5}	5.9×10^{-5}
167×10^3	123.0	0.9462	1.1×10^{-5}	9.9×10^{-5}
10^5	121.4	0.9350	0.81×10^{-5}	13.4×10^{-5}

(5) *Silver nitrate* (V). $\Lambda_{\infty} = 115.8$. $\rho 10.6 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
2222×10^3	110.5	0.9542	0.62×10^{-5}	0.89×10^{-5}
1852×10^3	109.5	0.9465	0.59×10^{-5}	0.88×10^{-5}
1031×10^3	107.4	0.9274	0.61×10^{-5}	1.15×10^{-5}
413×10^3	105.2	0.9084	0.68×10^{-5}	2.16×10^{-5}

(By trial).

(6) *Sodium nitrate* (K). $\Lambda_{\infty} = 105.3$. $\rho \ 23 \times 10^5$.

v c.c.	Λ .	α .	χ .	K .
10 ⁷	103.6	0.9836	0.48×10^{-5}	0.58×10^{-5}
5×10^6	102.7	0.9750	0.54×10^{-5}	0.71×10^{-5}
167×10^4	101.6	0.9646	0.67×10^{-5}	1.57×10^{-5}
10 ⁶	101.3	0.9617	0.74×10^{-5}	2.42×10^{-5}
5×10^5	100.1	0.9499	0.67×10^{-5}	3.63×10^{-5}
167×10^3	97.9	0.9295	0.53×10^{-5}	7.34×10^{-5}
10 ⁵	96.4	0.9152	0.48×10^{-5}	9.91×10^{-5}

(7) *Lithium nitrate* (F). $\Lambda_{\infty} = 95.2$. $\rho \ 20.9 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
512×10^3	90.0	0.9453	23×10^{-5}	31×10^{-5}
102×10^3	88.9	0.9338	45×10^{-5}	128×10^{-5}
51×10^3	88.0	0.9243	47×10^{-5}	220×10^{-5}
26×10^3	85.6	0.8991	38×10^{-5}	308×10^{-5}

(By trial).

(8) *Potassium iodide* (K). $\Lambda_{\infty} = 131.3$. $\rho \ 32 \times 10^5$.

v c.c.	Λ .	α .	χ .	K .
10 ⁷	129.3	0.9850	0.49×10^{-5}	0.64×10^{-5}
5×10^6	129.1	0.9837	0.71×10^{-5}	1.18×10^{-5}
167×10^4	128.5	0.9789	0.97×10^{-5}	2.71×10^{-5}
10 ⁶	127.9	0.9743	0.90×10^{-5}	3.69×10^{-5}
5×10^5	127.3	0.9698	0.87×10^{-5}	6.23×10^{-5}
167×10^3	125.0	0.9522	0.59×10^{-5}	11.80×10^{-5}
10 ⁵	123.4	0.9400	0.49×10^{-5}	14.72×10^{-5}

(9) *Potassium hydroxide* (K). $\Lambda_{\infty} = 239.0$. $\rho \ 28 \times 10^4$.

v c.c.	Λ .	α .	χ .	K .
10 ⁶	234.0	0.9791	3.6×10^{-5}	4.6×10^{-5}
5×10^5	233.0	0.9749	4.8×10^{-5}	7.5×10^{-5}
2×10^5	230.0	0.9623	5.3×10^{-5}	12.2×10^{-5}
10 ⁵	228.0	0.9539	5.6×10^{-5}	19.7×10^{-5}
5×10^4	225.0	0.9415	5.1×10^{-5}	30.3×10^{-5}
2×10^4	219.0	0.9163	3.6×10^{-5}	50.0×10^{-5}

(10) *Sodium hydroxide* (K). $\Lambda_{\infty} = 217.6$. $\rho \ 5 \times 10^5$.

v c.c.	Λ .	α .	χ .	K .
10 ⁶	208.0	0.9561	1.4×10^{-5}	2.08×10^{-5}
5×10^5	206.0	0.9469	1.5×10^{-5}	2.84×10^{-5}
2×10^5	203.0	0.9331	1.9×10^{-5}	6.50×10^{-5}
10 ⁵	200.0	0.9193	1.8×10^{-5}	10.48×10^{-5}
5×10^4	197.0	0.9056	1.7×10^{-5}	17.37×10^{-5}
2×10^4	190.0	0.8733	1.4×10^{-5}	30.09×10^{-5}

(11) *Hydrochloric acid* (K). $\Lambda_{\infty} = 383.4$. $\rho \ 13 \times 10^5$.

v c.c.	Λ .	α .	χ .	K .
10 ⁶	377.0	0.9832	3.2×10^{-5}	5.75×10^{-5}
5×10^5	376.0	0.9806	2.8×10^{-5}	9.91×10^{-5}
2×10^5	373.0	0.9728	2.3×10^{-5}	17.39×10^{-5}
10 ⁵	370.0	0.9652	1.9×10^{-5}	27.88×10^{-5}
5×10^4	367.0	0.9571	1.6×10^{-5}	42.23×10^{-5}
2×10^4	360.0	0.9391	3.2×10^{-5}	72.42×10^{-5}

(12) *Nitric acid* (K). $\Lambda_{\infty} = 379.8$. $\rho = 2.3 \times 10^5$.

<i>v</i> c.c.	Λ .	α .	χ	K .
10 ⁶	375.0	0.9874	6.3×10^{-5}	7.73×10^{-5}
5×10^5	374.0	0.9848	8.7×10^{-5}	12.76×10^{-5}
2×10^5	371.0	0.9769	9.7×10^{-5}	20.66×10^{-5}
10 ⁵	368.0	0.9690	9.4×10^{-5}	30.29×10^{-5}
5×10^4	364.0	0.9585	8.2×10^{-5}	44.22×10^{-5}
2×10^4	357.0	0.9400	6.3×10^{-5}	73.63×10^{-5}

Strong mineral acids and alkalis are peculiar in showing a maximum of equivalent conductivity at high dilution, the conductivity then diminishing with further dilution. In one case (Whetham and Paine, *Proc. Roy. Soc.*, 1908, *A*, **81**, 58; compare Kohlrausch and Maltby, *Wiss. Abh. der Physik tech. Reichsanstalt*, 1900, **3**, 199) (sulphuric acid) this has been shown to be due to basic impurities; the same explanation very probably applies to the other cases. The values in tables (9)—(12) have been taken from those portions of the experimental numbers which appeared to be least affected by this error. Considering the many sources of error in the conductivity measurements, and the very marked influence of these errors on the calculations, the constants agree remarkably well. The nearly constant value of ρ for a series of salts is noteworthy; ρ probably depends on the dielectric constant of the solvent and the mean free ionic path.

Summary.

1. The explanations which have been given to account for the failure of Ostwald's dilution law in the case of strongly ionised electrolytes are considered.

2. It is shown that Ostwald's dilution law, $\alpha^2/(1-\alpha)v = \text{constant}$, assumes that ionisation is a spontaneous reaction in the same sense as the thermal dissociation of a gas. Experiments on the ionisation of gases by Röntgen rays, etc., point to a strong ionising influence of the free ions themselves. Larmor has suggested that the ions in solutions of electrolytes may exert a similar influence. This leads to the substitution of the formula

$$\alpha^2/(v + \rho\alpha)(1-\alpha) = \text{constant}$$

instead of Ostwald's formula, the latter being deducible as a special case for weak electrolytes. This is shown to be in agreement with the conductivity data for twelve strongly ionised electrolytes in dilute solutions. ρ is a constant for each electrolyte at a given temperature.

3. The possibility of testing the fundamental hypothesis, by examining the effect of a magnetic field on the conductivity of an electrolyte, is suggested.

XCIX.—*A New Sulphide of Nitrogen.*

By FRANK PLAYFAIR BURT.

WHEN the yellow sulphide of nitrogen, N_4S_4 , is heated in a vacuum, it sublimes without decomposition. At 100° the vapour pressure is appreciable, and a sublimate soon makes its appearance when one end of an exhausted glass tube containing a little of the sulphide is heated in a steam-jacket.

In the course of some attempts to effect quantitative analysis of the vapour by means of silver gauze, it was observed that, whilst at temperatures above 200° decomposition was complete, very little action took place when the silver was kept at temperatures of 100 — 120° . Advantage was taken of this fact to remove the last traces of free sulphur from nitrogen sulphide.

Into a vertical glass tube about 1 cm. in diameter, 1—2 grams of powdered nitrogen sulphide were dropped, and a roll of silver gauze was pushed in above so as just to touch the sulphide. The tube was then drawn out 3—4 cm. beyond the top of the gauze, and attached by quill tubing to a mercury pump. After exhaustion in the cold, the vertical tube was heated in a steam-jacket up to the level of the top of the silver. The sulphide slowly volatilised, and the bulk of it deposited as a crystalline crust immediately above the silver. During the experiment the gauze was gradually covered with a film of silver sulphide, and a very small quantity of nitrogen was continuously evolved.

After a few hours' heating, when there was a conspicuous sublimate of the yellow sulphide, a faint blue film was observed lining the quill tubing leading to the pump. This film gradually increased in quantity and in extent in both directions. If the experiment was pushed sufficiently far, the blue deposit crept down the tube until it overlapped the crystals of yellow sulphide, forming an intermediate green zone, while it spread a foot or more along the quill tubing in the direction of the pump. The colour of the deposit increased to a fine, deep blue when viewed by transmitted light, until finally those portions of the tube which were most thickly coated became opaque. By reflected light, the colour was bronze, with a metallic lustre.

It should be noted here that the formation of a blue substance was observed by O. C. M. Davis when heating the compound $N_4S_4, SbCl_5$ in a vacuum, but the quantity obtained was too small to investigate.

When all the yellow sulphide had been sublimed, the tube was

cooled, air was let in, and the portion containing the blue substance was broken off for examination. The film was extremely thin, and yielded an unweighable quantity of bronze-coloured fluff when scraped out with a knife.

The substance was conveniently examined by treating with various reagents small pieces of quill tubing which were coated with the film. It was found to be quite insoluble when boiled with several organic liquids which dissolve the yellow sulphide, such as ether, chloroform, benzene, or carbon disulphide. On shaking or warming a piece of the tubing in water, the film rapidly scaled off, and was slowly decomposed. On adding a few drops of bromine water, solution was accelerated, and the resulting liquid gave a precipitate of barium sulphate when mixed with a solution of a barium salt.

When another portion was warmed with a solution of sodium hydroxide, ammonia was evolved.

When heated in air, the substance was decomposed with the evolution of vapours having an odour somewhat like that of iodine, and recalling that of a foul gun-barrel. This may have been due to the presence of the liquid sulphide of nitrogen, N_2S_5 , described by Muthmann and Clever (*Zeitsch. anorg. Chem.*, 1897, **13**, 200). When heated in a vacuum, the substance showed no signs of volatilising at 100° , and it could be freed in this manner from any accompanying yellow sulphide.

When a small quantity was heated in a melting-point tube, decomposition occurred without liquefaction, the substance turning yellow at about the melting point of the yellow sulphide (188°).

A small tube containing a few specks of the compound was exhausted and sealed up, and then rapidly heated to a temperature a few degrees below the melting point of the yellow sulphide in the vapour of boiling aniline. A blue ring was observed to creep up the tube in the wake of the rising aniline vapour, and when the tube was completely submerged, it was seen to be filled with a yellow vapour, which afterwards deposited as crystals on the cooling walls. On examining these crystals with a lens, two distinct types were seen to be present, one consisting of the small, highly refracting crystals characteristic of a sublimate of yellow sulphide of nitrogen, and the other of brown, feathery needles. There were also some milky patches that were probably sulphur. A little nitrogen was found in the tube when the end was broken under mercury.

Many unsuccessful attempts were made to obtain a quantity of the substance sufficient for analysis. The temperature of the silver was varied between 100° and 130° with apparently little effect.

When a very long column of silver gauze—about 100 cm.—was used, no blue compound at all was formed.

A weighable quantity was finally obtained by accident. Nitrogen sulphide was being sublimed in a vacuum over quartz wool, heated to about 300° ; analysis was by no means complete, and among a variety of products were some large, bronze-coloured crystals, which deposited in the connecting tubing leading to the pump. On examination these crystals proved to be identical with the blue substance already described. They broke with a bronze-coloured fracture, were insoluble in organic solvents, and gave the same odour on warming. A single large crystal, weighing about four milligrams, was selected for analysis. It was weighed in a small quartz bucket on an assay balance, and then introduced into a glass tube closed at one end; a small piece of silver gauze was pushed in above it, and the tube was drawn out and connected with a mercury pump by means of a sealed glass junction. After exhaustion, the silver gauze was heated with a naked flame, and the crystal was "sublimed" over it. The lower end of the gauze was coated with sulphide, and the nitrogen evolved was pumped off and transferred to a small constant-volume point gas-burette, where it was measured. The volume reduced to N.T.P. was 1.034 c.c. Taking the weight of a normal litre of nitrogen as 1.2514 grams, the

Weight of gas obtained	=	0.00129 gram
Weight of the crystal	=	0.00433 "
Weight of sulphur (by difference)	=	0.00304 "

Then, dividing by the respective atomic weights:

$$\begin{aligned}\text{Nitrogen} &= 129/14.01 = 9.21 \\ \text{Sulphur} &= 304/32.07 = 9.48\end{aligned}$$

showing a deviation of only 3 per cent. from the values required by a compound of the composition $(\text{NS})_x$, a satisfactory agreement in view of the very small quantity of material employed.

The new sulphide therefore contains the same relative proportions of nitrogen and sulphur as the yellow sulphide, and affords an interesting example of inorganic polymerism.

The mode of formation of this blue sulphide of nitrogen by the action of silver on the sulphide, N_4S_4 , is not easy to explain. Although its appearance is always accompanied by evolution of nitrogen and the formation of silver sulphide, any quantitative relationship between these phenomena is difficult to detect, because of the very small extent to which the reaction occurs. The fact that the blue sulphide is deposited beyond the yellow on a cooler part of the tube in spite of the demonstrably higher vapour pressure

of the latter suggests that the new sulphide is formed in situ from a volatile and unstable intermediate compound.

This hypothesis is supported by the following observations. Whenever the blue compound was being prepared, the phosphoric oxide between the reaction tube and the mercury pump acquired a red colour. This occurred even when the reaction tube was separated from the pump by many feet of connecting tubing, indicating the presence of a gas or vapour, which combined with or was decomposed by the phosphoric oxide. The red colour changed to green in the presence of air. The mercury in the pump chamber was also attacked. A U-tube cooled in liquid air and a mercury gauge were then introduced into the system. Besides the usual blue film, small quantities of a brown and a white substance were condensed in the U-tube in different zones. The white substance volatilised as soon as the liquid air was removed, and condensed again when the air was replaced, its vapour pressure being clearly indicated by the fall and rise of mercury in the gauge. When communication was established between the U-tube and the pump, with the liquid-air vessel removed, the phosphoric oxide was at once discoloured.

In another experiment the U-tube and its contents, while still cooled in liquid air, were sealed off after every trace of nitrogen had been pumped out. The blue film in the U-tube increased on keeping, and a little nitrogen was apparently formed. On the other hand, there was still something present which was condensible in liquid air after the tube had been kept for several days. It is possible that this was sulphur dioxide derived from the traces of oxygen which silver always contains.

The results of these experiments suggest that the immediate precursor of the blue sulphide of nitrogen is a gas or very volatile liquid at the ordinary temperature; that it contains relatively less sulphur, being formed from the yellow sulphide by partial reduction; and that it decomposes on keeping into the blue sulphide and nitrogen. These suggestions are put forward tentatively, because the amount of substance dealt with was so small that quantitative treatment was impossible.

It is at least probable that the sulphides of nitrogen may prove as numerous as their oxygen analogues.

In conclusion, I desire to thank Mr. F. L. Usher for assistance in the experiments and for many helpful suggestions.

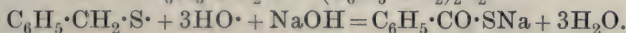
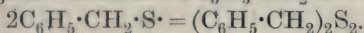
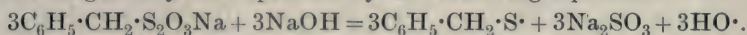
UNIVERSITY COLLEGE,
LONDON.

C.—*The Action of Sodium or Potassium Hydroxides on Sodium Alkyl Thiosulphates and on Disulphides.*

By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

FROMM AND ERFURT (*Ber.*, 1909, **42**, 3816) have recently criticised the authors' views with respect to the mechanism of the reaction between sodium hydroxide and sodium benzyl thiosulphate, and have expressed themselves as being in favour of Gutmann's idea (*Ber.*, 1908, **41**, 1650) that an intermediate compound, thiobenzyl hydroperoxide, $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{S}\cdot\text{OH}$, is formed. Their criticism is, however, to some extent based on a misconception of our views, so that it is necessary for us to refer to the subject again.

In our first communication on the subject (*Trans.*, 1908, **93**, 1396) we wrote: "It is found that three molecules of sodium benzyl thiosulphate react with approximately four molecules of sodium hydroxide, giving approximately one molecule of benzyl disulphide. The reaction is probably very complicated, but the chief stages may be expressed by the following equations:



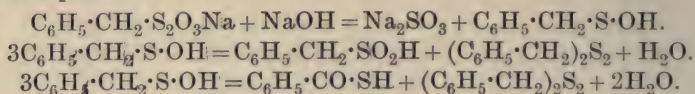
The third equation accounts for the fourth molecule of sodium hydroxide, but there are undoubtedly a number of subsidiary reactions which occur at the same time."

In a further communication to the *Berichte* (1908, **41**, 4376), in connexion with Fromm's proof (*Ber.*, 1908, **41**, 3397) that the so-called Gutmann's solution—prepared by the action of alcoholic potassium hydroxide on sodium ethyl thiosulphate—contains ethylsulphinic acid, we repeated the above equations, and amplified them by the following statement: "Dann verbinden sich zwei der $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{S}\cdot$ Reste mit einander zum Disulfid, während der dritte Rest durch den nascierenden Sauerstoff zu Thiobenzoessäure und Benzoessäure oxydiert wird." We also referred to the fact that we had shown (*loc. cit.*) that the action of Gutmann's solution on sodium arsenite and on a mixture of potassium cyanide and sulphide may be ascribed to the presence therein of ethyl disulphide. Indeed, Gutmann, in a footnote in his original paper, describes the isolation of an oil—which he supposed to be thioethyl hydroperoxide, but which we have shown to be ethyl disulphide—which gave the above-mentioned reactions with arsenite, cyanide, and sulphide. It is true that in another part of the paper (*loc. cit.*, p. 1651) Gutmann states that these reactions are due to thioethyl hydroperoxide,

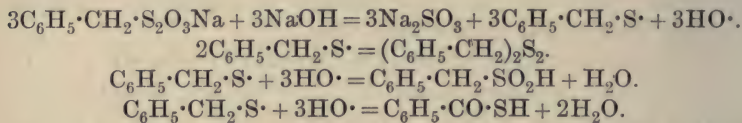
“oder ein aus diesem entstandener Körper,” but in all his later papers he ascribes various reactions to this hypothetical substance, and makes no mention of any product resulting from it.

It is only in connexion with these reactions with arsenite and a mixture of potassium cyanide and sulphide that we have hitherto ascribed oxidising properties to an organic disulphide. So far as the formation of benzoic and thiobenzoic acids—to which must also be added benzylsulphinic acid, according to Fromm and Erfurt—is concerned, we distinctly stated, as given above, that these acids are probably formed by the oxidation of a portion of the $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{S}\cdot$ residues by nascent oxygen (from the OH groups).

Since it has hitherto been impossible to isolate the hypothetical compound, thioethyl hydroperoxide (or any other thioalkyl hydroperoxide), we are of the opinion that its existence should not be postulated when the course of the reaction can be otherwise equally well explained. Thus, Fromm and Erfurt account for the action of sodium hydroxide on sodium benzyl thiosulphate by the following equations, thiobenzyl hydroperoxide being formed as an intermediate product:



The following equations give, however, an equally good explanation:

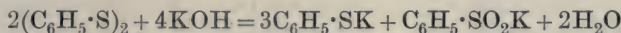


Fromm and Palma (*Ber.*, 1906, **39**, 3324) in an investigation on the oxides of hydrogen sulphide show that when sulphur is dissolved in alcoholic potassium hydroxide in the presence of benzyl chloride, the latter compound is partly oxidised to benzoic and thiobenzoic acids. They suggest that the oxidation may be due to the reaction represented by the equation $2\text{KOH} + \text{S} = \text{K}_2\text{S} + \text{H}_2\text{O} + \text{O}$, or else to the formation of an intermediate compound, K_2SO , analogous to K_2O_2 , which possesses strong oxidising properties. In a later paper (*Ber.*, 1908, **41**, 3405), Fromm expresses himself in favour of the second alternative, but it is a significant fact that all endeavours to isolate a derivative of this hypothetical intermediate compound from the reaction mixture have been unsuccessful. Nor has any better success attended the attempts to isolate derivatives of the various thioalkyl hydroperoxides from the different reaction mixtures. Until such attempts are successful we do not see that any

advantage is to be gained at present by postulating the existence of these hypothetical intermediate products.

In our previous papers on the subject we have pointed out that some of the discrepancies between our results and those obtained by Gutmann may be due to the fact that the latter worked with alcoholic solutions, whereas we used aqueous solutions. Any disulphide formed, being insoluble in water, is not further acted on by the aqueous sodium or potassium hydroxide, a fact which has been further confirmed by Fromm and Erfurt in the case of benzyl disulphide. We also pointed out (Trans., 1908, **93**, 1398) that benzyl disulphide is attacked by alcoholic potassium hydroxide, and further experiments have confirmed this.

In investigating the action of alcoholic potassium hydroxide on disulphides, Fromm and his co-workers have made extensive use of benzyl chloride for the characterisation of the reaction products. Thus, in proving that phenyl disulphide is decomposed according to the equation :



(Ber., 1908, **41**, 3403), the reaction was carried out in the presence of benzyl chloride, and the formation of the mercaptan and the sulphinic acid demonstrated by the isolation of phenyl benzyl sulphide and phenyl benzyl sulphone. They have further found that the products of reaction may vary with the proportions of reagents used. For example, when *p*-nitrophenyl disulphide was treated with an excess of both sodium hydroxide and benzyl chloride in alcoholic solution, the products of reaction were simply *p*-nitrophenyl benzyl sulphide and benzoic acid. When insufficient benzyl chloride was taken, the substances formed were *p*-nitrophenyl benzyl sulphide and *p*-nitrophenylsulphinic acid,* the reaction having taken place in accordance with an equation similar to the one given for the phenyl disulphide. Furthermore, when the *p*-nitrophenyl disulphide was heated with excess of alcoholic sodium hydroxide alone, *p*-nitrophenyl mercaptan was formed, and also a substance, insoluble in alkali, which could not be characterised, but which was not considered to be a primary decomposition product of the disulphide.

In the case of benzyl disulphide we have found that the products of reaction are different, according as benzyl chloride is present from the beginning or not. When the disulphide is first heated with alcoholic potassium hydroxide, and the reaction mixture then treated with benzyl chloride, the only substances we have been able

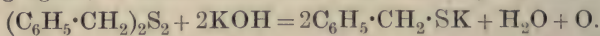
* The difference between these two results is possibly due to the excess of benzyl chloride in the first case being more readily oxidised to benzoic acid than the $\text{NO}_2\cdot\text{C}_6\text{H}_4\text{S}\cdot$ residue to the corresponding sulphinic acid.

to identify are benzyl sulphide and benzoic acid. The reaction apparently takes place according to some such equation * as the following:



On the other hand, when the disulphide is heated with the alcoholic potassium hydroxide and the benzyl chloride together, the products of reaction are benzyl sulphide, the benzylmercaptal of benzaldehyde, and benzoic acid. In no case have we been able definitely to prove the formation of benzylsulphinic acid.

The explanation of the formation of the benzylmercaptal of benzaldehyde may possibly be as follows: The benzyl disulphide, in the presence of the alcoholic potassium hydroxide, acts as an oxidising agent, in accordance with the following equation:



The benzyl chloride is thereby oxidised to benzaldehyde,† which then couples with the benzyl mercaptan, with the formation of the corresponding mercaptal. The difficulty in connexion with this explanation is that the mercaptals are usually formed from the mercaptan and aldehyde in an acid solution, and we have furthermore found that benzyl mercaptan and benzaldehyde, when heated together with alcoholic potassium hydroxide, do not give the mercaptal; practically all the mercaptan is recovered unchanged. It is possible, however, that when the mercaptal is formed from the disulphide, the reaction may be analogous to the so-called nascent reactions, the $\text{C}_6\text{H}_5\cdot\text{CH}_2\cdot\text{S}\cdot$ residues coupling with the $\text{C}_6\text{H}_5\cdot\text{CH}\cdot$ residue from the benzyl chloride. This would be in agreement with the formation of stilbene by passing the vapours of benzyl chloride over heated soda-lime (*Annalen*, 1866, **139**, 314), and of 2:2'-dinitrostilbene by the action of alcoholic potassium hydroxide on *o*-nitrobenzyl chloride (*Ber.*, 1888, **21**, 2072; compare also Nef, *Annalen*, 1897, **298**, 257, for complete literature references). The alternative explanation, to the effect that the benzyl chloride contained benzylidene chloride, was shown to be untenable, by analysis of the benzyl chloride.

Since benzyl disulphide is readily decomposed by alcoholic potassium hydroxide, one would expect a similar reaction to take place in the case of ethyl disulphide. If this were so, it would follow that the reactions of Gutmann's solution with arsenite and with a mixture of potassium cyanide and sulphide could not be

* Such equations can only be considered as approximate ones, representing the formation of the main products of reaction.

† It will be seen in the experimental part that some benzaldehyde is produced during the reaction.

due to the presence of ethyl disulphide. We have shown, however (*loc. cit.*), that ethyl disulphide can be isolated from Gutmann's solution. Moreover, further experiments have shown that when either sodium ethyl thiosulphate or ethyl disulphide are heated with an excess of alcoholic potassium hydroxide under reflux for several hours, the dark-coloured solution so obtained still gives the reaction with the mixture of cyanide and sulphide, so that it apparently still contains some ethyl disulphide which has escaped decomposition, possibly because of its volatility.* After such prolonged heating at the temperature of boiling alcoholic potassium hydroxide, it is improbable that the solution would contain the unstable thioethyl hydroperoxide postulated by Gutmann and Fromm. In support of this we find that when ethyl disulphide is heated for several hours with alcoholic potassium hydroxide in a sealed tube at 150—180°, the product obtained no longer gives the reaction with the mixture of cyanide and sulphide.

EXPERIMENTAL.

In order to test the purity of the benzyl chloride used, a weighed quantity was treated with an excess of sodium thiosulphate in aqueous-alcoholic solution for three days at the ordinary temperature; the excess of thiosulphate was then determined by titration with iodine (compare Slaton and Twiss, *Trans.*, 1909, **95**: 93):

0.4128 gram C_7H_7Cl required 32.0 c.c. $N/10-Na_2S_2O_3 =$
 $C_7H_7Cl : 0.98Na_2S_2O_3.$

Benzylidene chloride does not react with sodium thiosulphate, so that the above figures indicate the purity of the benzyl chloride.

Action of Alcoholic Potassium Hydroxide on Benzyl Disulphide in the Absence of Benzyl Chloride.

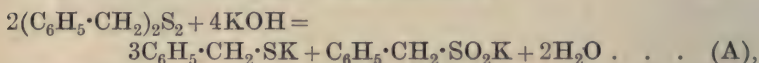
A mixture of 5.3 grams (1 mol.) of benzyl disulphide and 6.5 grams (5.4 mols.) of potassium hydroxide, dissolved in 50 c.c. of 95 per cent. alcohol, was heated for one hour under reflux, a deep red liquid being obtained. Nine grams (3.3 mols.) of benzyl chloride were then added, and the heating was continued for another hour; the colour faded to a light brownish-yellow, and much potassium chloride separated. The alcohol and the excess of benzyl chloride were then distilled off in a current of steam,† and the residual

* The fact that ethyl disulphide is formed by the interaction of alcoholic potassium hydroxide and sodium ethyl thiosulphate would seem to indicate that the velocity of coupling of the $C_2H_5S\cdot$ -residues is greater than the velocity with which ethyl disulphide is decomposed by the alkali.

† Benzyl monosulphide is slightly volatile with steam, so that a little is lost in this operation.

liquid, when cold, was extracted with ether. After drying and removal of the ether, the extract was distilled under diminished pressure. There were only a few drops of distillate, possessing an odour of benzaldehyde, below 170° ; the bulk distilled at $170\text{--}175^{\circ}/13$ mm., and proved to be benzyl monosulphide. After recrystallisation from alcohol, it melted at $49\text{--}50^{\circ}$. A small amount of a tarry, uncrystallisable liquid remained in the distilling flask at the end of the distillation. The alkaline liquid remaining after the extraction with ether was acidified and again extracted with ether, when benzoic acid was obtained. After sublimation it melted at 121° .

5.3 Grams (1 mol.) of benzyl disulphide gave 8.20 grams (1.78 mols.) of benzyl monosulphide and 0.63 gram (0.24 mol.) of benzoic acid. The residue in the flask weighed 1.25 grams. If the reaction had proceeded according to the equation:



1 molecule of disulphide should have given at the most 1.5 molecules of monosulphide after the treatment with benzyl chloride; benzyl sulphone (from the benzylsulphinic acid) should also have been produced in appreciable quantity, but we were unable to detect any, although, of course, there may have been a little present in the tarry residue in the distilling flask. If the reaction took place according to the equation:



1 molecule of disulphide should give 1.8 molecules of monosulphide and 0.2 molecule of benzoic acid, which agrees approximately with the experimental results, although it takes no account of the residue in the distilling flask.

In another experiment, 7.5 grams (1 mol.) of benzyl disulphide gave 11.85 grams (1.83 mols.) of benzyl monosulphide, the residue in the distilling flask weighing 1.35 grams; the yield of benzoic acid was not determined.

Action of Alcoholic Potassium Hydroxide on Benzyl Disulphide in the Presence of Benzyl Chloride.

In order to test whether the reaction proceeded according to equation A in the presence of benzyl chloride, a method similar to that adopted by Fromm in the case of phenyl disulphide was used (*Ber.*, 1908, **41**, 3403). A mixture of 5 grams (2 mols.) of benzyl disulphide, 6 grams (10.5 mols.) of potassium hydroxide, and 3.8

grams (3 mols.) of benzyl chloride,* dissolved in 50 c.c. of 95 per cent. alcohol, was heated under reflux. The mixture turned deep red as soon as the heating was started; at the end of an hour it was filtered, while hot, from the potassium chloride which had separated. No crystals separating from the filtrate on cooling, water was added in excess, causing the separation of an oil, and the whole was extracted with ether. The red ethereal solution so obtained, after drying and evaporating off the ether, gave a red residue, which partly crystallised on standing. The paste of crystals so obtained was dried on a porous tile, and after recrystallisation from alcohol gave crystals of benzyl monosulphide, melting at 49—50°. The alkaline liquid remaining after the extraction with ether was heated on the water-bath to expel the ether, 3 c.c. of benzyl chloride and enough alcohol to give a clear solution added, and the whole heated under reflux for one hour; the resulting mixture was then distilled in a current of steam to remove the excess of benzyl chloride, and finally extracted with ether. From the ethereal extract the only product which could be isolated was benzyl monosulphide; no evidence was obtained of the formation of benzyl sulphone. The alkaline liquid remaining from the steam distillation and extraction with ether was acidified, and again extracted with ether. The ethereal extract contained benzoic acid.

The above operations were repeated several times. In one case double the quantities given above were taken, and the mixture kept for ten days at the ordinary temperature, as it was thought that any sulphinic acid formed might have been destroyed by heating with the excess of potassium hydroxide. The subsequent treatment was then as above. In another experiment the reaction mixture was 6 grams (2 mols.) of benzyl disulphide, 4.5 grams (6.6 mols.) of potassium hydroxide, and 3.8 grams (2.5 mols.) of benzyl chloride. In all cases, however, the results were similar to those already detailed, no sulphone being isolated in any experiment.

In order to be certain that our methods of working were satisfactory, we have repeated Fromm's experiments on the action of aqueous sodium hydroxide on sodium benzyl thiosulphate, and in each case we have readily obtained the sulphone.

The paste of crystals which was obtained in every case from the first ethereal extract evidently did not consist solely of benzyl monosulphide. Consequently, the porous tiles which had been used to dry the paste were finely powdered and extracted with ether.

* This is sufficient benzyl chloride to transform the benzyl mercaptan into benzyl monosulphide, but insufficient to form the sulphone from the benzylsulphinic acid, if the latter is present.

From the ethereal extract was obtained a red oil, which almost completely crystallised on long keeping. The crystals were dried on a porous tile, and, after recrystallisation from alcohol, long, colourless needles were obtained, which melted at 62° (see below). Tangible quantities of the red colouring matter could not be obtained for further investigation.

Larger quantities of the crystals melting at 62° were obtained as follows. A mixture of 15 grams (2 mols.) of benzyl disulphide, 18 grams (10.6 mols.) of potassium hydroxide, and 30 c.c. (8 mols.) of benzyl chloride,* dissolved in 150 c.c. of alcohol, was heated under reflux. A vigorous reaction occurred at first, and a red colour was formed, only to disappear again very quickly. After heating for one hour, the reaction mixture was distilled in a current of steam in order to remove the alcohol and excess of benzyl chloride. It was then extracted with ether, and again extracted after acidifying. The acid extract once more yielded benzoic acid.

The first extract, after removal of the ether, was distilled under diminished pressure. The distillate, which passed over below $170^{\circ}/13$ mm., was variable in quantity, according as the previous steam distillation had been more or less thorough. In most cases only one or two drops of distillate were obtained below 170° , but in one case a few c.c. were obtained; on redistillation under atmospheric pressure they gave a distillate containing benzyl chloride and benzaldehyde,† whilst a residue containing stilbene (m. p. 124° after recrystallisation from alcohol) remained in the distilling flask, the stilbene probably resulting from thermal decomposition of a little benzyl monosulphide present (compare Forst, *Annalen*, 1875, **178**, 370). The main portion of the distillate passed over at 170 — $175^{\circ}/13$ mm., and consisted of benzyl monosulphide. The residue in the flask solidified on cooling, and, after recrystallisation from alcohol, gave long needles melting at 62° , which were identified as the benzylmercaptal of benzaldehyde:

Disulphide.	Monosulphide.	Mercaptal.
15 grams, 1 mol.	13 grams, 1 mol.	10.8 grams, 0.53 mol.
7 „ 1 „	4.4 „ 0.72 „	5.0 „ 0.52 „

The mercaptal was identified by analysis, oxidation to the sulphone, and by determination of its molecular weight. It has been previously prepared by Fromm and Junius (*Ber.*, 1895, **28**, 1102), who give the melting point as 64° . After several recrystallisations the melting point of our product still remained at 62° . Also, a specimen which we prepared by the action of benzyl mercaptan on benzaldehyde in alcoholic solution in the presence of

* This gives an excess of both potassium hydroxide and benzyl chloride.

† Proved by preparation of the hydrazone.

hydrogen chloride melted at 62° . (Found, $C=74.9$; $H=6.4$; $S=18.8$. Calc., $C=75.0$; $H=6.0$; $S=19.0$ per cent.)

Determination of the molecular weight in benzene by the cryoscopic method gave the following figures:

Weight of benzene = 16.57 grams.

Weight of mercaptal.	Δt .	M.W.
0.1880	-0.180°	315
0.2445	-0.229	322
0.4925	-0.454	327

$C_{21}H_{20}S_2$ requires M.W. = 336.

Oxidation in glacial acetic acid solution with excess of 30 per cent. hydrogen peroxide (compare Hinsberg, *Ber.*, 1910, **43**, 289), or by means of permanganate, gave the disulphide, which, after recrystallisation, melted at 215° : Laves (*Ber.*, 1892, **25**, 347) gives 213° .

Action of Alcoholic Potassium Hydroxide on Sodium Ethyl Thiosulphate and Ethyl Disulphide.

Five grams of sodium ethyl thiosulphate were heated with a solution of 4 grams of potassium hydroxide under reflux for six hours. The dark-coloured liquid so obtained had an odour which was neither that of the pure mercaptan nor of the pure disulphide. On boiling with a solution of potassium cyanide and sodium sulphide, thiocyanate was formed, since after acidification with hydrochloric acid and addition of ferric chloride there was an immediate red coloration.

Similar results were obtained when 3.5 grams of ethyl disulphide were heated with a solution of 3 grams of potassium hydroxide under reflux for six hours. When, however, a mixture of 2 grams of ethyl disulphide, 4 grams of potassium hydroxide, and 6 c.c. of alcohol was heated in a sealed tube at $150-180^{\circ}$ for seven hours, the resulting product gave no thiocyanate when heated with cyanide and sulphide.

We desire to express our thanks to the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of the foregoing investigation.

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CI.—A Study of the Landsberger-Sakurai Boiling-point Method of Determining Molecular Weights.

By WILLIAM ERNEST STEPHEN TURNER.

So convenient is the Landsberger-Sakurai boiling-point method of determining molecular weights, that it is no matter of surprise to find that quite a number of investigators have introduced modifications with the view of extending its use and applicability. These modifications have been of a varied character. Thus, whilst Sakurai, the originator of the method of heating the solution by a stream of vapour issuing from the boiling solvent (Trans., 1892, **61**, 994), placed the solution under examination in a U-tube set in an air-bath, maintaining the latter at a suitable temperature with a gas burner, Landsberger* (*Ber.*, 1898, **31**, 461) constructed the simple and well-known form consisting of boiling tube and vapour mantle.

Walker and Lumsden (Trans., 1898, **73**, 502) graduated the boiling tube and introduced the method of reading the volume of the solution as an alternative to finding the weight of the solvent. McCoy (*Amer. Chem. J.*, 1900, **23**, 353), C. N. Riiber (*Ber.*, 1901, **34**, 1060), Ludlam (Trans., 1902, **81**, 1193), Beckmann (*Zeitsch. physikal. Chem.*, 1902, **40**, 129), and A. Lehner (*Ber.*, 1903, **36**, 1105) have departed considerably from the original form, the essential difference being the insertion, in all these designs, of the molecular-weight tube within the boiler which supplies the current of vapour. Finally, by using a Weinhold vacuum vessel as the boiling tube, Erdmann and Unruh (*Zeitsch. anorg. Chem.*, 1902, **32**, 413) were able to dispense with a vapour mantle.

A glance at the publications of the investigators named reveals the satisfactory nature of the results obtained, and suggests that, with a stricter attention to the elimination of errors, the Landsberger-Sakurai method, which has very considerable advantages over the ordinary Beckmann method in regard to speed, and in the absence of superheating of the solution, might be capable of being employed, not only in the investigation of substances of normal molecular weight in solution, but also in the study of substances the molecular weight of which alters with change of concentration.

Whilst much attention, however, has been devoted to the design of apparatus, less consideration has hitherto been paid to checking the errors inherent in the method. As a consequence, series of

* Meyer and Jaeger (*Ber.*, 1903, **36**, 1555) have described a modification of the Landsberger method so as to permit the use of hygroscopic solvents.

determinations, extending over a considerable range of dilution, have not been generally attempted, and would indeed, if carried out, be untrustworthy.

In an earlier communication, dealing with the work done in conjunction with Dr. A. N. Meldrum on molecular complexities of amides in various solvents (Meldrum and Turner, *Trans.*, 1908, **93**, 876), a brief account of the errors of the Lumsden-Walker method was recorded. A form of apparatus which has already been used with success in some three hundred series of molecular weight determinations, some of which will presently be communicated, is now described, together with the necessary working details.

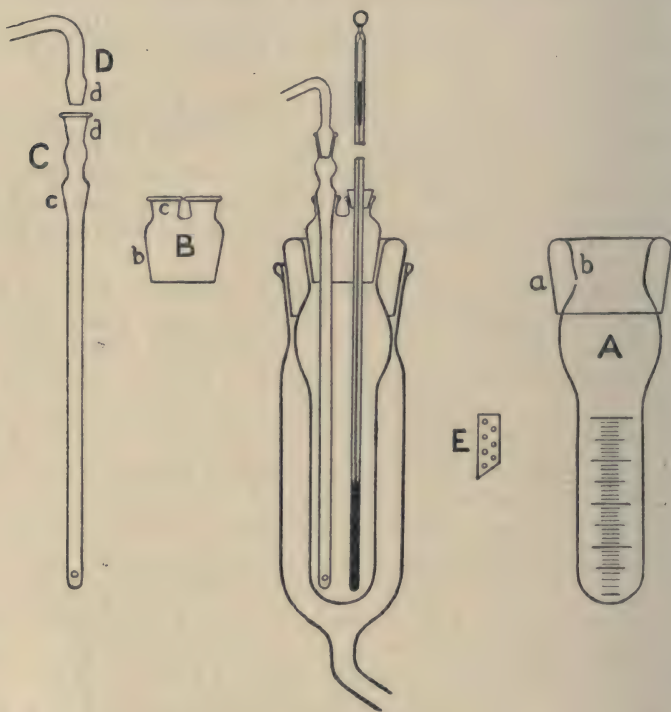
Most of the investigators who have used the Landsberger-Sakurai principle have, in the main, also followed Walker and Lumsden in measuring the volume of the solution, instead of the weight of solvent, and the forms of apparatus devised have been such that the weight determination can only be carried out indirectly or with inconvenience.

The author's apparatus follows the original Landsberger form, for whilst there would be little difficulty in placing the molecular weight tube within the boiler, the arrangement of a boiler external to the measuring apparatus and mantle is simpler and more convenient to work. The essential difference between the form used by the author and that of Landsberger lies in the introduction of glass joints, such that the parts can be rapidly detached and again restored to their original positions, and the measuring tube can be weighed together with the vapour tube and thermometer.

In the diagram the small letters indicate the ground glass parts which fit. *A* is the boiling tube, provided with a flange, and graduated either in c.c. or by divisions at a fixed distance apart. The dimensions of the tube most frequently used are: length 17 cm.; internal diameters, at the mouth 3.8 cm., tube below the bulb 3.2 cm. Smaller tubes have been employed, and have given equally satisfactory results, and economised in the amount of solute and solvent used. *B* is the stopper with two tubulures, of which one is ground to fit the stopper of the vapour delivery tube *C*, and the other plain for the thermometer, which is fastened in position by a small cork. The tube *D* leads to the boiling vessel, and should be inclined to allow condensed solvent to return to the boiler. Too great a distance between the source of vapour and the tube *C* should be avoided, a distance of 15—20 cm. between the limbs of the vapour tube being convenient. To diminish condensation, the exposed parts of the vapour tube are wrapped round with a long strip of asbestos paper, and condensation of vapour within the

measuring tube is much reduced by enclosing the outer jacket in a cylinder made from asbestos paper, the cylinder resting on a disk of asbestos millboard encircling the upper part of the exit tube at the base of the outer jacket. A duster may be folded loosely across the stopper during a determination.

E is a short piece of glass tubing, perforated with a dozen holes, and cut off at an angle so as to rest on the bottom of the measuring tube and protect the thermometer bulb, which it envelops, from



the current of vapour. Its use is unnecessary if the rate at which vapour enters is carefully regulated, but it serves as an additional protection.

A screen of asbestos millboard or wire gauze should be placed between the boiler and the measuring apparatus.

The thermometer used was specially designed for the apparatus, and is a differential one, somewhat similar to that described by Beckmann (*Zeitsch. physikal. Chem.*, 1905, 51, 342, Fig. 34), the stem being of stout capillary tubing, of diameter 8 mm., with scale engraved on the stem. Its length is 40 cm. only, against the

52 cm. of the Beckmann instrument; its scale is divided into $1/50$ ths of a degree, and as the length of scale per degree is equal to that on the Beckmann thermometer, it is easy, with a little experience, to read to a thousandth of a degree. Before use, the instrument, with the scale exposed, was carefully calibrated, at different temperatures, against thermometers standardised on the hydrogen scale, and the following corrections were used: 1° on the differential instrument equals, at 55° , 1.015; 60° , 1.020; 80° , 1.025; 100° , 1.030. These corrections are somewhat less than those needed for the ordinary Beckmann thermometer.

The Boiling Point of the Solvent.

A flame of constant height should be used below the boiler, and may be obtained by using a Bunsen burner fitted with air and gas regulator, the latter being adjusted when the gas supply is turned on full; or the device of Sakurai (*loc. cit.*) may be used.

The amount of solvent placed in the measuring tube initially should be such that when the reading of the boiling point is taken, the thermometer bulb is covered with liquid. Vapour should be passed in at a rate sufficient to cause a steady drip from the condenser, and although the rate of distillation varies somewhat with the solvent, it should always be possible to count the separate drops. Too great a rate of flow of vapour will slightly cool the thermometer bulb. This cooling effect comes into evidence when the boiling is interrupted, the temperature immediately rising by three to six thousandths of a degree, and then remaining constant for two or three seconds. Probably this cooling effect is the same in each reading, but it is to be avoided by regulation of the vapour stream, and by adoption of the protective arrangement for the thermometer bulb.

The thermometer speedily attains a steady state, generally within three to five minutes after boiling has begun, and the temperature may be read. As will be understood from the corrections mentioned below, the temperature never remains stationary in the case of the solvent, but creeps upward at a very slow rate, owing to gradual condensation of liquid within the measuring tube, and the consequent increase of pressure due to the increased head of liquid. This upward creep in the space of a minute is only noticeable in the case of a liquid like benzene, which condenses easily, and in all cases the thermometer registers the boiling point corresponding with the particular height of liquid in the measuring tube.

The temperature having been registered, the boiler and measuring tube are removed from position, connexion broken at *d*, the stopper

B raised,* and the liquid level read in order that subsequent boiling points may be reduced to this level.

The table below illustrates the accuracy with which a determination of boiling point may be made. Chloroform, on account of its high density and its instability, is not one of the easiest solvents to employ, and an illustration of its use will serve well to indicate the accuracy of which the method is capable.

To indicate the conditions of comparison, the original barometric height in each experiment is given under P , since the tests extended over several days. The values under T are the readings on the differential thermometer of the boiling points, corrected both for barometric height and for pressure of the liquid column in the tube. The conditions prevailing during the first experiment of each series were taken as standard:

<i>Series I.</i>		<i>Series II.</i>	
Chloroform distilled at 61·360—61·380°/763·90 mm.		Chloroform distilled at 61·345—61·360°/763·85—763·90 mm.	
P (mm.).	T .	P (mm.).	T .
1. 745·25	1·600	1. 760·70	2·145
2. 745·35	1·602	2. 760·80	2·152
3. 745·20	1·598	3. 760·80	2·145
4. 735·65	1·620	4. 761·25	2·143
5. 735·25	1·618	5. 761·60	2·133
		6. 761·75	2·133
		7. 763·55	2·151

The correction for change of barometric height was deduced from Regnault's boiling-point determinations as 1 mm. = 0·044°, but this value probably holds accurately over a very short range only. It will be noted, however, that where the comparisons were made under nearly equal barometric pressures, the boiling points agree closely. It is probable, also, that any cause affecting the boiling point of the solvent will alter the boiling point of the solution in the same direction.

The Boiling Point of the Solution.

The behaviour of the thermometer after reaching the steady state, which is very rapidly arrived at, varies with the solvent and the concentration of the solution. In the case of a solution of high molecular concentration, the temperature reaches a maximum,

* If the thermometer is maintained always in the same position, the molecular-weight tube can be calibrated with the vapour tube and thermometer dipping into the liquid. There is then no need to raise the stopper, and the tube can be kept closed throughout the experiment.

remains constant for perhaps a minute, and then slowly falls, owing to the gradual dilution of the solution by the further condensation of vapour. Such behaviour is noticeable with the solvents benzene and alcohol. Experience has shown, however, that the thermometer is at each stage in equilibrium with the solution, provided the maximum point has once been attained.

With increase of dilution, the time taken by the thermometer to acquire the steady state gradually increases, while the effect of the condensation of vapour in turn diminishes, and the temperature may remain constant for some time. When very dilute solutions are under investigation, the temperature may, after a time, creep upwards if the rise of boiling point due to increased pressure is greater than the fall corresponding with the dilution of the solution. Such cases are rare, but have been noticed by the author when dealing with substances of very high molecular weight dissolved in a dense solvent, such as chloroform.

Water and ether condense but slowly, and it is sometimes necessary to add solvent to the solution to bring about a sufficient state of dilution. According to Ludlam (*loc. cit.*), carbon disulphide behaves similarly. Acetone, chloroform, and alcohol are easy to use; benzene condenses more readily, but still allows of readings at four dilutions. A longer tube might also be useful with this last-named solvent.

In connexion with water, it may be remarked that it is best to empty the boiler after each reading, shake out previously used broken porous tile, and then restore the water and fresh tile.

After the determination of boiling point, the apparatus is disconnected, and when the level of the liquid has been read, the tube, with stopper and accessories, is placed in a sling and weighed rapidly to a centigram. If the volumes corresponding with the tube graduations are known, alternative methods of calculating the results are available.

The Errors of the Method.

1. Unless the solvent is pure and of fairly constant boiling point, fractionation may occur, and the boiling point rise with time. The solvent should be purified and dried, and is best fractionated through a Young's eight-pear still-head, the distillate being separated into portions differing in boiling point by 0.02 — 0.03° , or less, where possible. Very little, if any, change will then occur during the distillation within the molecular weight apparatus, and should any change occur, the correction necessary is probably included in (3) below, assuming that the alteration of boiling point is proportional to the amount of liquid distilled.

2. If, following Walker and Lumsden, the volume of the solution is measured instead of the weight of solvent—and most of the investigators previously mentioned have adopted this method—the results obtained, certainly in fairly strong solutions, are only approximate; for Lumsden (*Trans.*, 1907, **91**, 24) has demonstrated that, save in aqueous solution, a substance has the same, or nearly the same, volume as it possesses, at the same temperature, in the liquid state, and, further, in practice, the molecular elevation of boiling point is deduced from experiments in which the weight of solvent, and not the volume of solution, is the adopted standard. The author's apparatus has, therefore, been devised so that the weight of solvent can be determined, in addition to the volume.

It not infrequently occurs that of the two series of molecular-weight results, calculated by volume and by weight respectively, the volume method gives values closer to the formula weight than does the weight method. Two considerations may account for this apparent superiority of the volume method. It must be remembered, in the first place, that, since it is difficult to find two substances, acting as solute and solvent respectively, which are quite indifferent to one another, as indicated by entire absence of volume and temperature change on admixture, the molecular elevation of boiling point used in practice is only an average number, and a substance yielding, by the weight method, constant but high molecular weight results will probably, by the volume method, afford apparently more correct results. Again, if a substance under investigation has molecules which are associated, not only will the volume method yield lower results, but the increase of molecular association with increasing concentration will be less than when the weight method is employed.

The difference between the two methods of calculating the results will be illustrated in another communication. In sufficiently dilute solution there is practically no difference between the two methods.

3. The boiling point increases as the pressure of liquid in the measuring tube becomes greater, and the consequences of the error involved may be considerable. The second series of results with the chloroform solution of diphenyl recorded later (p. 1192) is worked up here to illustrate the differences between a corrected and the two possible uncorrected series. Two determinations of the boiling point, with the solvent at different heights, were carried out. Under I the results are given when the boiling point of the solvent at the lower level is the standard; under II, the higher level standard is adopted. $C=39.0$; $(C_6H_5)_2=154$.

Height of liquid.		Temp. correction.		Δ (corr.).	M. W.		
I.	II.	I.	II.		I.	II.	Corr.
(Solvent) 19.6	28.5	—	—	—	—	—	—
(Solution) 11.0		+0.046	+0.093	0.745	165	176	154
15.1		+0.024	0.071	0.594	162	177	153
20.0		-0.002	0.045	0.479	154	170	154
24.4		-0.025	0.022	0.389	149	168	150

The method of establishing the requisite correction has already been given (Meldrum and Turner, *loc. cit.*). Experience has shown that whilst the actual correcting factor is, in the main, dependent on the density of the liquid involved, it nevertheless does not agree with the calculated value. It differs, for example, with the diameter of the tube, being smaller in a wide than in a narrow tube, a difference due partly, but not wholly, to the greater proportion of space taken up in the smaller tube by the vapour tube and thermometer. Moreover, it is easily possible that two other corrections are included in what is, at first sight, a correction for the effect of pressure on the boiling point, namely, corrections for slight fractionation of the liquid, as mentioned under (1), and for the effect of increasing hydrostatic pressure on the thermometer bulb.

As in the previous communication, the figures given below indicate the correction per tube division of 2 mm., and the series of results quoted illustrate the accuracy of the determinations, which, save those with chloroform, depended on differences of boiling point only of two to four hundredths of a degree:

Alcohol.		Acetone.		Benzene.	
0.0017	0.0019	0.0019	0.0025	0.0028	0.0028
0.0015	0.0019	0.0021	0.0017	0.0021	0.0024
0.0017	0.0018	0.0017	0.0022	0.0026	0.0026
0.0015	0.0015	—	—	0.0035	—
Mean values 0.0017°		0.0020°		0.0027°	

Eleven determinations with chloroform made in an apparatus of the same size previously used (Meldrum and Turner, *loc. cit.*) yielded results varying between 0.0055° and 0.0067° per division, thus confirming the earlier figure obtained with the use of a less sensitive thermometer. In the apparatus now described, the correcting factor is roughly a third less.

4. If the stream of vapour entering the measuring tube is too rapid, a cooling of the thermometer bulb occurs. The exclusion of this error has been dealt with above.

5. The weight of solvent is liable to a small correction due to the amount of solvent present, either in the state of vapour, or as

liquid draining back into the solution from the walls of the apparatus. An approximate determination of this correction can be made by measuring both volume and weight at the boiling point of the solvent, converting the volume into weight by the aid of the known specific gravity and subtracting the result from the weight directly obtained. The correction for alcohol is about 0.2 gram; for benzene, 0.3 gram.

The Molecular Boiling-point Elevation of Chloroform.

During an extended use of the solvent chloroform, it was found that the calculated values of the molecular weights of substances which, from all other evidence, were expected to agree with the formula weight were consistently low, and a revision of the boiling-point constant was undertaken. Beckmann originally gave the figure 36.6 (*Zeitsch. physikal. Chem.*, 1890, **6**, 437); revised the data and substituted the number 35.9 (*ibid.*, 1895, **18**, 473), and reverted to the earlier constant later on (*ibid.*, 1902, **40**, 129). In a recent investigation (*ibid.*, 1908, **63**, 177), of which the author was unaware until his own verification was being carried out, Beckmann has arrived, as the result of very carefully executed experiments, at the much higher value of 39.0. As solutes, Beckmann used benzil, camphor, and naphthalene, one series only being given with the last-named substance among the eight from which the final result was deduced. The author has employed in his own tests the substances diphenylamine, diphenyl, anthracene, and methylacetanilide. The higher number is fully confirmed.

Solute: *Diphenylamine*, M.W. = 169.1.

I.				II.			
<i>w</i> (gram).	<i>W</i> (grams).	Δ .	<i>C</i> .	<i>w</i> (gram).	<i>W</i> (grams).	Δ .	<i>C</i> .
1.150	42.82	0.618	38.9	0.989	44.40	0.502	38.1
1.150	53.57	0.498	39.2	0.989	53.30	0.423	38.5
1.150	64.17	0.418	39.4	0.989	63.13	0.361	39.0
				0.989	70.05	0.324	38.8
Mean = 39.2				Mean = 38.6			

Solute: *Diphenyl*, M.W. = 154.1.

I.				II.			
0.899	31.65	0.697	37.9	0.903	30.60	0.745	39.0
0.899	38.97	0.578	38.7	0.903	38.07	0.594	38.7
0.899	60.50	0.366	38.0	0.903	47.62	0.479	39.0
0.899	70.55	0.308	37.3	0.903	57.15	0.389	38.0
Mean = 38.0				Mean = 38.7			

III. Mean of a third series = 37.8.

Solute: *Anthracene*, M.W.=178.1.

I.				II.			
<i>w</i> (gram).	<i>W</i> (grams).	Δ .	<i>C</i> .	<i>w</i> (gram).	<i>W</i> (grams).	Δ .	<i>C</i> .
0.996	35.05	0.646	40.5	1.0475	41.20	0.559	38.3
0.996	42.85	0.527	40.4	1.0475	50.30	0.455	38.0
0.996	51.95	0.436	40.5	1.0475	61.38	0.376	38.5
0.996	62.02	0.368	40.3				
Mean = 40.4				Mean = 38.3			

III. Mean of a third series = 38.2.

Solute: *Methylacetanilide*, M.W.=149.1.

I.				II.			
1.628	51.72	0.821	38.9	0.9245	30.48	0.816	40.1
1.628	59.92	0.709	38.9	0.9245	38.68	0.657	41.0
1.628	69.17	0.601	38.0	0.9245	51.38	0.491	40.7
				0.9245	65.23	0.382	40.2
Mean = 38.6				Mean = 40.5			

III. Mean of a third series = 40.3.

General mean: $C = 39.0$.

The author desires to express his thanks to the Government Grant Committee of the Royal Society for a grant which provided part of the cost of constructing the apparatus.

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CII.—*The Influence of Radium Emanation on Equilibrium in a Gaseous System: a Correction.*

By FRANCIS LAWRY USHER.

IN a paper which has recently appeared (this vol., p. 389), the velocity constant for the decomposition of ammonia by emanation was calculated on the erroneous supposition that the expression $-\frac{dC_t}{dt} = kC_t k' E_t$ is incapable of strict integration.

Mr. H. T. Tizard has been so good as to point out this mistake, and has recalculated the velocity constant from my experimental data for experiments I—III (pp. 393—394) according to the correct formula:

$$\frac{1}{E_0 - E_t} \cdot \log \frac{V_0}{2V_0 - V_t} = K,$$

where V refers to the volume at N.T.P. of the reaction mixture, and not to the volume of ammonia. The following tables should therefore take the place of the three tables on pp. 393 and 394.

Experiment I.

Time in days.	$\log \frac{V_o}{2V_o - V_t}$	$E_o - E_t$	K
0	0	0	—
0·56	0·02853	0·096	0·297
0·77	0·04093	0·129	0·317
1·56	0·06966	0·244	0·235
1·83	0·07558	0·280	0·270
2·58	0·09922	0·371	0·268
4·54	0·12294	0·558	0·220
5·54	0·15077	0·630	0·238
7·56	0·16714	0·743	0·225
9·67	0·17628	0·824	0·214
12·58	0·18034	0·896	0·201
40·00	0·21397	0·999	0·214

Experiment II.

Time in days.	$\log \frac{V_o}{2V_o - V_t}$	$E_o - E_t$	K
0	0	0	—
0·042	0·00260	0·008	0·325
0·083	0·00665	0·015	0·443
0·104	0·00737	0·019	0·388
0·135	0·00905	0·024	0·377
0·191	0·01147	0·034	0·337
0·865	0·05655	0·144	0·392
1·031	0·06632	0·169	0·392
1·198	0·07773	0·194	0·401
1·854	0·11202	0·283	0·396
2·042	0·12439	0·307	0·405
2·185	0·13103	0·325	0·403
2·840	0·16104	0·400	0·403
3·230	0·17527	0·440	0·398
3·840	0·19586	0·498	0·393
3·958	0·19995	0·509	0·393
5·840	0·25101	0·650	0·386
6·896	0·27298	0·710	0·384
7·840	0·28235	0·755	0·374
8·840	0·29751	0·795	0·374
9·840	0·30601	0·829	0·369
12·886	0·32006	0·901	0·355
36·000	0·35437	0·998	0·354

Experiment III.

Time in days.	$\log \frac{V_o}{2V_o - V_t}$	$E_o - E_t$	K
0	0	0	—
0·031	0·00239	0·006	0·398
0·073	0·00674	0·013	0·518
0·76	0·06591	0·128	0·515
1·08	0·09227	0·176	0·524
1·75	0·13639	0·270	0·505
2·08	0·15922	0·312	0·510
2·78	0·19438	0·393	0·494
3·75	0·23675	0·490	0·483
4·75	0·26571	0·574	0·463
6·75	0·31412	0·703	0·447
7·76	0·32408	0·752	0·431
8·75	0·33428	0·792	0·422
9·75	0·33842	0·826	0·410
10·76	0·34578	0·855	0·403
11·76	0·35759	0·879	0·407
13·77	0·35759	0·916	0·390
14·76	0·38107	0·929	0·410
15·76	0·35759	0·941	0·380
32·00	0·37310	0·997	0·374

The corrected values of K are fairly satisfactory, and would no doubt be much improved if a correction for gas driven into the glass could be applied; even without this, the constancy of K is sufficient to justify the assumptions which were made, namely, that the velocity of decomposition is proportional to the concentration of ammonia and to the amount of emanation present at time t .

It follows from this that the attempt which was made (p. 398)

to correct the velocity constant for a supposed alteration of the efficiency of the emanation with time was unnecessary. On the other hand, it is true that the amount of decomposition possible is a direct function of the ratio of ammonia to emanation molecules, if this ratio is less than 134,000:1.

The volume-percentage of ammonia in equilibrium with its decomposition products at 15°, calculated by the revised formula given by Nernst in a recent paper (*Zeitsch. Elektrochem.*, 1910, 16, 96), is about 98, and this gives additional support to the view that the action of the emanation is not catalytic. It may also be pointed out that, although the room-temperature varied during the experiments within rather wide limits—about 8°—the velocity constant shows no corresponding irregularities, as would be the case if the reaction were being catalysed.

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CIII.—*Some Reactions of Benzyl Mercaptan. Benzyl Tri- and Tetra-sulphides.*

By JOHN ARMSTRONG SMYTHE and AQUILA FORSTER.

THE attempted synthesis of organic polysulphides by the condensation of mercaptans and sulfoxides, which led to the detailed examination of the action of hydrochloric acid on benzyl sulfoxide, and was described in a recent paper by one of us (Smythe, *Trans.*, 1909, 95, 349), has been continued. Some results of this study form the subject of the present communication. The tri- and tetra-sulphides of benzyl have been isolated, benzyl disulfoxide has been shown to be capable of easy reduction by benzyl mercaptan and hydrogen sulphide, and further illustrations of the reducing properties of mercaptan have been furnished by its reactions with sulphur dioxide and benzyl disulfoxide.

EXPERIMENTAL.

Action of Sulphur Dioxide on Benzyl Mercaptan. Benzyl Trisulphide.

A convenient amount of benzyl mercaptan (b. p. 195°) is dissolved in about seven times its volume of glacial acetic acid, and the liquid saturated simultaneously with sulphur dioxide and hydrogen chloride, the gases being passed in at intervals for several days. No apparent reaction takes place at first, but after a lapse of time,

varying from a few days to a week or two, the odour of mercaptan disappears, and, occasionally, a white, crystalline mass is precipitated. The product is then distilled in a current of steam, whereby impurities in the mercaptan are removed; the non-volatile residue, after solidification and drying, is fractionally crystallised from alcohol, to which enough ethyl acetate is added to prevent precipitation of oil. In this way it is resolved into two components, which prove to be benzyl disulphide and benzyl trisulphide.

Benzyl disulphide melts at 71° ; on analysis:

0.1016 gave 0.2540 CO_2 and 0.0550 H_2O . $\text{C}=68.20$; $\text{H}=6.02$.

0.1258 „ 0.2386 BaSO_4 . $\text{S}=26.04$.

M.W. (by cryoscopic method) = 233.

$\text{C}_{14}\text{H}_{14}\text{S}_2$ requires $\text{C}=68.30$; $\text{H}=5.69$; $\text{S}=26.04$ per cent.

M.W. = 246.

Benzyl trisulphide melts at 49° , and crystallises well from alcohol and ethyl acetate in long, thin laths, apparently monoclinic, which sometimes attain a length of an inch or more. These have a strongly developed cleavage, and flatten under the spatula somewhat like fibrous ammonium chloride. The compound is excessively soluble in benzene. It may be noted that its melting point is the same as that of the monosulphide. Analysis yielded the following results:

0.1882 gave 0.4166 CO_2 and 0.0874 H_2O . $\text{C}=60.35$; $\text{H}=5.16$.

0.1983 „ 0.4982 BaSO_4 . $\text{S}=34.46$.

M.W. (by cryoscopic method) = 268.

$\text{C}_{14}\text{H}_{14}\text{S}_3$ requires $\text{C}=60.40$; $\text{H}=5.02$; $\text{S}=34.58$ per cent.

M.W. = 278.

When solutions in alcohol of benzyl trisulphide and silver nitrate are mixed, a crystalline compound is precipitated. The reaction takes place even in very dilute (0.5 per cent.) solution. The compound crystallises from boiling absolute alcohol in pure white needles, which are unstable in contact with the mother liquor, but can be kept for a long time without darkening in a dry atmosphere. These crystals melt and decompose suddenly at 96° , the residue turning brownish-red. The substance appears to be an *additive compound* of silver nitrate and the trisulphide:

0.2396 gave 0.0578 Ag. $\text{Ag}=24.13$.

$\text{C}_{14}\text{H}_{14}\text{S}_3, \text{AgNO}_3$ requires $\text{Ag}=24.08$ per cent.

In respect to the formation and composition of this compound, the trisulphide thus resembles the disulphide of benzyl.

Attempts have been made to determine the relative quantities of di- and tri-sulphide, the only organic products formed by the action of sulphur dioxide on benzyl mercaptan, the method adopted for

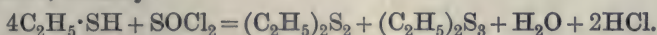
their separation being that of fractional crystallisation. In view of the great number of crystallisations necessary to effect a satisfactory separation, the results can only be regarded as approximate, although they are doubtless accurate enough for the purpose in hand. In one experiment, 30 grams of benzyl mercaptan yielded 24.3 grams of solid products, and these were resolved into 9.6 grams of disulphide and 9.8 grams of trisulphide, leaving an unresolved mixture of these weighing 1.5 grams (loss = 3.4 grams). In another case, 67.7 grams of solid products yielded 31.6 grams of disulphide, 30.4 grams of trisulphide, and 0.6 gram unresolved (loss = 5.1 gram).

It is clear, then, from these figures, that the di- and tri-sulphides are formed in, practically, the same amounts, and the following equation expressing the reaction may be regarded as quantitative:

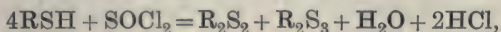


It may be remarked, incidentally, that this reaction furnishes an interesting example of the oxidising properties of sulphur dioxide.

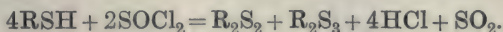
Holmberg, who has lately studied the action of thionyl chloride on ethyl mercaptan (*Annalen*, 1907, **359**, 81), gives evidence to show that, having regard to the organic compounds, the reaction is quantitative and expressible by an equation quite analogous to the one above, namely:



The action of thionyl chloride on phenyl mercaptan has been investigated more recently by Tasker and Jones (*Trans.*, 1909, **95**, 1910), who, led by the observation that sulphur dioxide is given off during the reaction, have proposed various equations involving the formation of sulphur, sulphur suboxide, and phenyl tetrasulphide, although there is no direct evidence of the production of any of these compounds. These authors appear to have overlooked the obvious fact that the sulphur dioxide proceeds from the decomposition of thionyl chloride by the water formed during the reaction. Supposing that all the water were decomposed in this way, then Holmberg's general equation, expressing the reaction between thionyl chloride and mercaptans, namely:



would become



Leaving out of consideration the small amount of secondary reaction between sulphur dioxide and mercaptan which would be possible under the conditions of experiment, then all reactions between thionyl chloride and mercaptan should take place between the limits set by these two equations. The determinations by Tasker and Jones of the total titre (mercaptan, thionyl chloride,

hydrochloric acid, and sulphur dioxide) with standard iodine and alkali for varying quantities of phenyl mercaptan and thionyl chloride confirm this statement, although they furnish no evidence, as these authors seem to think, for the formation of phenyl tetrasulphide (*loc. cit.*, p. 1914, equation A).

There is thus no reason to think that phenyl mercaptan behaves towards thionyl chloride differently from ethyl mercaptan, and it seems likely that sulphur dioxide and thionyl chloride react in a similar manner with all mercaptans.

Action of Sulphur Chloride on Benzyl Mercaptan.

Benzyl tetrasulphide has been prepared by Holmberg's method (*Annalen*, 1908, **359**, 81) as follows. Five grams of freshly distilled sulphur chloride (b. p. 135°), dissolved in 25 c.c. of carbon tetrachloride, were added slowly to a solution of 12 grams of benzyl mercaptan in 50 c.c. of carbon tetrachloride, the mixture being well cooled. A violent reaction set in, and much hydrogen chloride was evolved. On distilling in a current of steam, carbon tetrachloride and excess of mercaptan were removed, and an amber-coloured oil remained, which solidified on keeping. On crystallisation from alcohol, this product was obtained as a white, crystalline powder, melting at $49-50^{\circ}$. Analysis proved this to be *benzyl tetrasulphide*:

0.2150 gave 0.4294 CO_2 and 0.0990 H_2O . C = 54.46; H = 5.11.

0.2618 „ 0.5243 CO_2 „ 0.1134 H_2O . C = 54.61; H = 4.83.

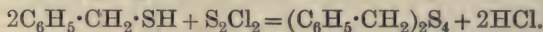
0.1012 „ 0.3097 BaSO_4 . S = 41.93.

M.W. (by cryoscopic method) = 310.

$\text{C}_{14}\text{H}_{14}\text{S}_4$ requires C = 54.19; H = 4.52; S = 41.29 per cent.

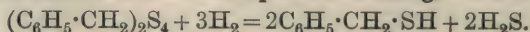
M.W. = 310.

The yield in the above reaction is 10.4 grams, which is practically quantitative, on the assumption that the equation of reaction is as follows, and having regard to the amount of sulphur chloride taken:

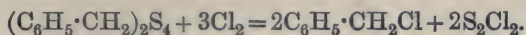


It is essential, in preparing the tetrasulphide, that the mercaptan should be in considerable excess and the reagents well diluted, otherwise dark-coloured oils, difficult to handle, are produced.

When a solution of the tetrasulphide in acetic acid is treated with zinc dust, hydrogen sulphide is evolved, and on distilling the product in a current of steam, an oil passes over which is readily identified by its odour and its reaction with iodine, whereby benzyl disulphide, m. p. 71° , is produced, as benzyl mercaptan. It is evident that the reduction takes place according to the equation:



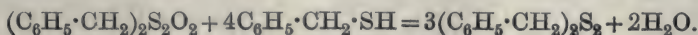
Chlorine attacks the tetrasulphide in solution of carbon tetrachloride, sulphur chloride and benzyl chloride being produced. The solution in the tetrachloride was saturated in the cold with dry chlorine, and then heated for some hours under reflux to remove excess of chlorine. On distilling the product, at first under diminished and then under atmospheric pressure, two fractions were obtained, boiling at 130° and 179° respectively. The former was proved to be sulphur chloride by the reaction with water; the latter, on treatment with alcoholic solution of sodium sulphide, gave sodium chloride and benzyl sulphide (m. p. 49°), and was thus shown to be benzyl chloride. The reaction may thus be expressed by the equation:



Benzyl tetrasulphide does not react with methyl iodide, whereby it differs from the monosulphide; and it does not form an additive compound with silver nitrate, being distinguished in this respect from the di- and tri-sulphides. It is not oxidised by nitric acid (D 1·3). Both the tri- and tetra-sulphides are oxidised by hydrogen peroxide. It is hoped that experiments on this subject at present in progress will throw some light on the constitution of these compounds. As the first four sulphides of benzyl have now been prepared, it is not without interest to note their melting points, which are given in order from the mono- to the tetra-sulphide, namely, 49° , 71° , 49° , $49\text{--}50^{\circ}$.

Action of Benzyl Mercaptan on Benzyl Disulphoxide.

3·9 Grams of benzyl disulphoxide and 8·8 grams of benzyl mercaptan were dissolved in glacial acetic acid, and the solution saturated with hydrogen chloride. After a few days, a sudden reaction set in with evolution of heat, and, on cooling, crystals were deposited from the solution. The acids and the excess of mercaptan were now removed by distillation in a current of steam. The residue weighed 9·8 grams, and was found to be a simple substance, melting at 71° after recrystallisation, and giving the characteristic reaction for benzyl disulphide with silver nitrate. A determination of sulphur further proves it to be the disulphide. (Found, S=26·39. Calc., S=26·10 per cent.) It seems clear that reaction has taken place in the manner expressed by the equation:

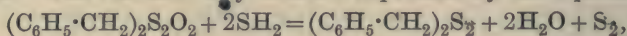


This is confirmed by the yield of disulphide, which is 94 per cent. of that required by the equation.

Hydrogen sulphide reacts in a similar way to mercaptan, reducing

benzyl disulphoxide to disulphide, and being itself oxidised to sulphur.

Eight grams of the disulphoxide were dissolved in glacial acetic acid and saturated simultaneously with hydrogen chloride and hydrogen sulphide. After keeping some days, the product was distilled in a current of steam, and the residue, after solidification, was extracted with alcohol. This dissolved out 7.1 grams of a compound melting at 71° , and giving the reactions characteristic of benzyl disulphide, and the insoluble portion was recognised as sulphur. The reaction may thus be expressed by the equation:



and in agreement with this, the yield is 92 per cent. of that required by the equation.

Similar reactions have been tried with benzyl sulphone and benzyl sulfoxide, but without success; the conditions, however, in the latter case are necessarily somewhat different, since hydrogen chloride has to be replaced by other condensing agents owing to its action on the sulfoxide (Trans., 1909, **95**, 349).

The authors' best thanks are due to Mr. H. Tiplady, B.Sc., for help in the preparation of benzyl trisulphide.

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CIV.—*Apparatus for Demonstrating the Volumetric Compositions of Gases.*

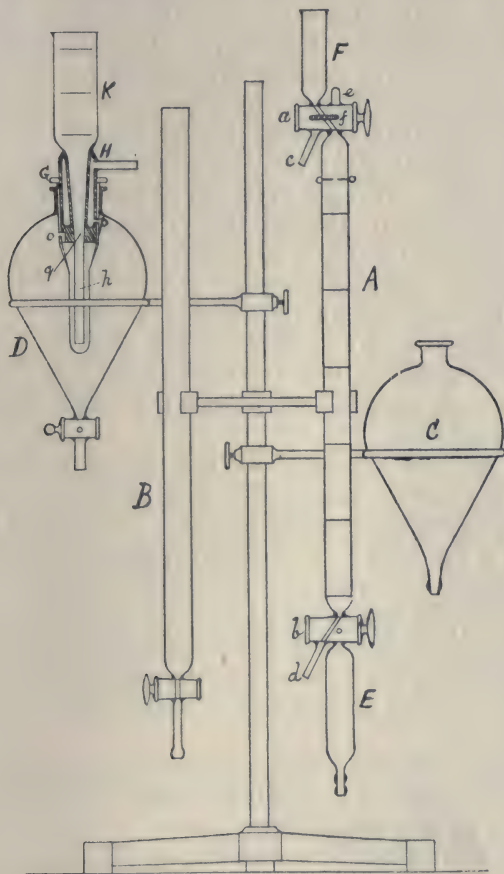
By ALARIC VINCENT COLPOYS FENBY.

THE apparatus to be described has been devised to facilitate the demonstration of the combining volumes of gases by a quick and accurate method under such conditions that there is no necessity to correct the volumes for changes of temperature and pressure. The measurements are further simplified by using volumes of the gases which are simple multiples of one division on the gas burette.

The apparatus, as shown by the figure, consists of the following parts: (1) the gas burette *A*, (2) the levelling tube *B*, (3) the reservoir *C*, for filling the burette, and (4) a gas holder or generator *D*, for measuring known volumes of a gas into the burette. These parts can be supported on a single stand as shown.

The burette *A* is fitted with two taps, *a*, *b*, and the space between

the taps is divided into six equal parts (each 15 c.c.), with a small free space above the tap *b*. The tap *a* is fitted with a cup *F*, a tube *c* for a gas inlet, and a draining tube *e*, which is bent down behind the tap. By means of the oblique bore, the cup *F* can be connected to the burette, and by a half-turn of the tap the tubes *c* and *e* can be connected. To connect *F* to the tube *e*, a slot *f* is



cut in the side of the cone of the tap; this slot also serves to connect the tube *c* to the burette tube when gas is to be passed in through the tube *c*. The tap *b* enables the burette to be connected to the gas trap *E* and reservoir *C*, which is connected to *E* by rubber tubing, and also to the tube *d*, which is connected to the levelling tube *B*. Platinum electrodes are provided for sparking the gases.

A general description of the uses of the several parts will now be given to avoid repetition when referring to experiments later on.

I. In experiments in which chlorine is required, this gas is generated in the burette.

The levelling tube *B* is first partly filled with dilute hydrochloric acid or brine solution, whichever is necessary, and, to displace air from the connecting tube, some of the liquid is run into the bottom of the burette, and the tap *b* closed. The liquid in the burette is then run out through *E*. The reservoir *C* is connected to *E*, and filled with a clear, strong solution of bleaching powder. By raising *C* the burette is filled with the solution, and the tap *a* is closed. *C* is then lowered to its support. Strong hydrochloric acid is put into *F*, and by opening the tap *a* is allowed to enter the burette in small quantities. A rapid evolution of gas takes place, and the solution is forced down the burette. The pressure of the liquid in *C* prevents the too rapid expulsion of the bleaching powder solution. Usually chlorine collects in the trap *E* before the burette is completely filled, but by raising and lowering *C*, this gas is forced into the burette and displaces the acidified solution. The tap *b* is then closed. In this way the burette is readily filled with chlorine free from admixed air without the disagreeable escape of chlorine into the room.

The gas is then adjusted to the requisite volume under atmospheric pressure by opening the tap *a* to the air by the tube *c*, and expelling gas by the levelling tube *B*. The taps are then closed.

II. When a gas such as oxygen is required, it is introduced by filling the burette with water, and connecting the tube *c* to the gas-holder or generating apparatus, *c* being opened to the air through *e* for a while to expel air from the connecting tubes. The tube *c* is then connected to the burette, and the gas passed in by lowering the reservoir *C*. The volume and pressure are then adjusted by the levelling tube.

III. The gas required for mixture with chlorine, oxygen, or other gas in the burette is obtained from *D*, which may be used as a generator or as a gas-holder.

This apparatus consists of a wide-necked container with a tap at the bottom. The neck is fitted with a tube *G*, closed at its lower end. A hollow stopper *H*, through which a tube *h* is sealed, fits into the tube *G*. The tube *h* reaches nearly to the bottom of *G*, and above opens into the funnel or cup *K*. The stopper *H* is provided with an exit-tube, communicating with the container through a port *p*. The tube *G* opens to the container by a port *o*, and a passage cut in the base of the stopper *H*. By turning *H*, these two port-holes are closed. A third port *q* (not shown in the

figure) is drilled in the tube *G*, on the same level as *o*, which enables *K* to be opened to the container, while the ports *o*, *p*, are closed. To fill *D* with hydrogen, granulated zinc is placed in *D*, which is nearly filled with dilute acid. The tubes *G* and *H*, filled to the level *o* with water, are inserted, and some gas is allowed to escape by *q*. A tube dipping into a beaker is attached to the tap of the container. The cup *K* is turned a little to close *q*, and the liquid is forced out by opening the lower tap. When the generator is filled with gas, the excess of acid is removed by washing. This is done by filling *K* with water, and opening *o* and *p*. Gas is displaced through the stopper, expelling air from it, and when sufficient water has entered, the port *q* is opened, and the lower tap. Fresh water can then be passed through from *K* until the acid is removed, and *q* can be closed.

To use *D* as a gas-holder, it is filled with water, and the tube *G* and cup *K*, filled with water, are inserted. The tube from the gas supply is connected to a tube passing through a cork in the cup *K*. The port *q* is opened, and the water allowed to flow out by the lower tap. When the container is filled with gas, the tap is closed, and the port *q* shut off.

To transfer gas to the burette, the gas-holder is connected by narrow tubing to the side-tube *c* of the burette. The tube *c* is then connected to *e*, and some gas expelled to remove air from the tube by pouring water into *K* and opening *o* and *p*. The water level falls to level of *o*. By turning the tap *a*, the tube *c* is put in connexion with the burette by the passage *f*. The ports *o* and *p* being closed, water is poured into *K*, which is graduated from the level *o* into three parts, each equal to one division of the burette tube. By filling to the proper mark with water, a fixed volume of gas can be expelled under atmospheric pressure, the levelling tube, opened to the burette, being lowered as the gas enters. The levels are adjusted when the desired volume mark on the burette is reached. The taps are then closed, and the gas-holder disconnected. A measured volume of gas is thus introduced into the burette under atmospheric pressure. A description of an experiment will now be given.

Combination of Hydrogen and Chlorine.

The tube *B* is partly filled with a saturated solution of salt, boiled to expel air, and cooled. The burette is filled with chlorine, and the volume adjusted to the third division, as follows. A little of the salt solution is run into the burette, expelling some of the gas. The taps are closed, and the burette tilted backwards and forwards several times to dissolve some of the gas. More salt

solution is then allowed to enter, and the shaking repeated, and this is continued until the volume is reduced to about three and a-half divisions. The solution is now saturated, and the excess of gas is expelled and pressure adjusted. Hydrogen is now introduced from the generator *D*, as explained above, and the total volume adjusted to the lowest mark. While passing in hydrogen, the burette is screened from direct light by a loose-fitting cylinder of black paper or cardboard, the bottom only being exposed to show the level at the lowest mark. By this means the volume can be accurately adjusted. The gases are mixed by tilting the tube several times, and the screen is removed. The tube *B* is filled up with salt solution, and opened to the burette. The gases are readily exploded by burning a few inches of magnesium ribbon near the tube. A sharp click is heard, a cloud appears in the burette, and the salt solution enters and nearly fills the tube. The tube is tilted several times to dissolve completely the hydrochloric acid, and the pressure adjusted. A small residue of air remains, containing some chlorine. The chlorine is removed by adding aqueous potassium hydroxide from the cup *F*.

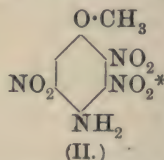
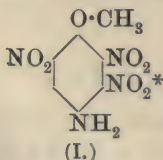
The apparatus can be used for the following experiments: Combining volumes of hydrogen and oxygen, composition of ammonia by the chlorine method, composition of carbon monoxide, compositions of the simple hydrocarbon gases, and decomposition of hydrogen chloride by sodium amalgam.

THE WYGGESTON SCHOOL,
LEICESTER.

CV.—*The Products of Diazotisation of the Trinitro-p-anisidines.*

By RAPHAEL MELDOLA and FRÉDÉRIC REVERDIN.

Two trinitro-derivatives of *p*-anisidine are theoretically possible:

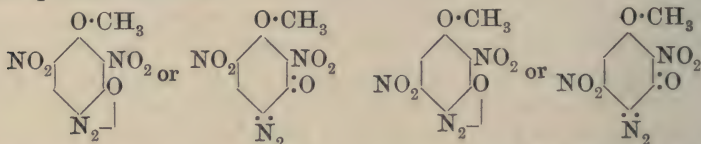


Of these the first was prepared by the nitration of the benzoyl derivative of *p*-anisidine (Reverdin and A. de Luc, *Arch. Sci. phys. nat.*, 1909, 27, 383), and the second by the methylation of the silver salt of the corresponding trinitroacetylaminophenol (Meldola and

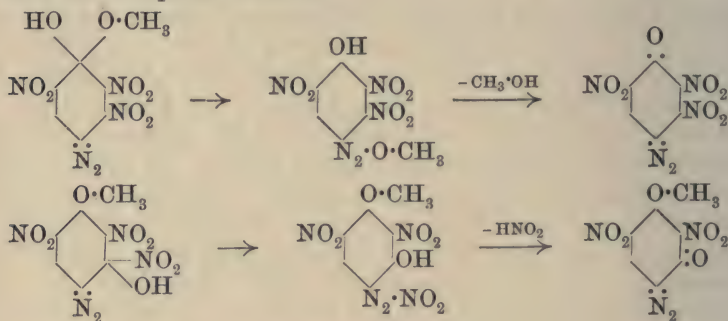
Kuntzen, *Trans.*, 1910, **97**, 455). In view of the mobility of the nitro-group in certain nitroamino-compounds on diazotisation, a comparative study of these trinitroanisidines appeared to be of special interest, and the present research was undertaken with the object of obtaining definite information concerning the special influence of the methoxy-group in determining such mobility. From the results made known in former papers, it appears that the nitro-group (*) in the above formulæ complies with all the conditions requisite to insure mobility, being in the ortho-position with respect to the diazotisable amino-group, and having another nitro-group in the ortho-position with respect to itself. A comparative study of the products of diazotisation of 2:3-dinitro-4-aminophenol and its methyl ether has shown that the influence of the methoxy-group is predominant, the formation of a paraquinonediazide being prevented in the latter case (Meldola and Hay, *Trans.*, 1907, **91**, 1477; also Meldola and Eyre, *Trans.*, 1902, **81**, 988). The ortho-quinone-diazide is accordingly formed under these conditions by the displacement of the ortho-nitro-group, whereas in the dinitroaminophenol itself, from which a para-quinonediazide can be obtained, no elimination of a nitro-group takes place. On the other hand, it has been shown that a methoxy-group in the para-position with respect to the diazotisable amino-group and in the ortho-position with respect to one or two nitro-groups is eliminated on diazotisation (Meldola and Stephens, *Trans.*, 1905, **87**, 1205; Reverdin and Bucky, *Ber.*, 1906, **39**, 2691). The existing state of knowledge concerning the configurations favourable respectively for the elimination of a nitro-group or of a methoxy-group was summarised in a former paper (Meldola and Hay, *Trans.*, 1907, **91**, 1474), and it has since been shown that in the trinitroaminophenol corresponding with No. II of the above formulæ, the trinitroquinonediazide is at once formed on diazotisation, no nitro-group being eliminated (Meldola and Hay, *Trans.*, 1909, **95**, 1383). The trinitroaminophenol corresponding with formula No. I has not yet been obtained, but this might also be expected to give a trinitroquinonediazide on diazotisation.

On comparing the formulæ of the two trinitroanisidines, it will be seen, in accordance with the general results of former researches, that not only is the nitro-group in both compounds in a favourable position for displacement, but that the methoxy-group is also in what may be called a critical position, and more especially in No. I, in which this group is between two ortho-nitro-groups and in the para-position with respect to the diazo-group. This pair of isomerides is therefore particularly suitable for determining the relative mobility of the nitro- and methoxy-groups under the

influence of a diazo-group. As will be seen from the experimental results, the question is answered decisively, both compounds losing the 3-nitro-group on diazotisation and giving rise to the dinitro-ortho-quinonediazides:



It is thus shown that under conditions equally favourable for the elimination of a nitro-group and a methoxy-group, the former is the more readily displaced when the diazo-group is formed in its neighbourhood. If the mechanism of the progress is expressed in terms of the hypothesis of "isomeric change," it may be said that the predominating influence is in favour of the second and not the first of the two possible schemes:



EXPERIMENTAL.

The diazotisation of the trinitroanisidines was effected in the usual way by dissolving the compounds in cold sulphuric acid, diluting with a little water, and adding solid sodium nitrite to the solution cooled in ice. On pouring the solution of diazonium sulphate into water, decomposition at once takes place, and the quinone-diazide is precipitated as a yellow, crystalline deposit.

2: 5-Dinitro-1-methoxy-3: 4-quinonediazide.

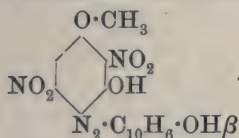
The compound prepared as above, after being washed and dried, was crystallised from hot glacial acetic acid. It is a fairly stable substance, crystallising in yellow prisms, melting and decomposing at 191—194°:

0.2277 gave 46 c.c. N_2 (moist) at 16° and 757.5 mm. $N = 23.47$.

$C_7H_4O_6N_4$ requires $N = 23.34$ per cent.

The compound is not explosive, but deflagrates on heating. It

combines slowly with β -naphthol in alkaline solution to form an azo-compound, which crystallises from boiling glacial acetic acid in brick-red needles, having a slight metallic lustre, and melting at 236° . From its mode of formation its constitution is:



0.0780 gave 9.9 c.c. N_2 (moist) at 17.5° and 764.1 mm. $\text{N}=14.78$.

$\text{C}_{17}\text{H}_{12}\text{O}_7\text{N}_4$ requires $\text{N}=14.58$ per cent.

The azo-compound is slightly phenolic, dissolving in dilute aqueous sodium hydroxide with a red colour. It is insoluble in cold alcohol, and very sparingly soluble in boiling alcohol. Its solution in concentrated sulphuric acid is violet, becoming redder on dilution with water.

2: 6-Dinitro-1-methoxy-3: 4-quinonediazide.

This compound was obtained by crystallisation from hot glacial acetic acid in orange prisms, melting at $197\text{--}198^\circ$. It deflagrates like its isomeride on heating:

0.0708 gave 14.35 c.c. N_2 (moist) at 16.8° and 755.8 mm. $\text{N}=23.41$.

$\text{C}_7\text{H}_4\text{O}_6\text{N}_4$ requires $\text{N}=23.34$ per cent.

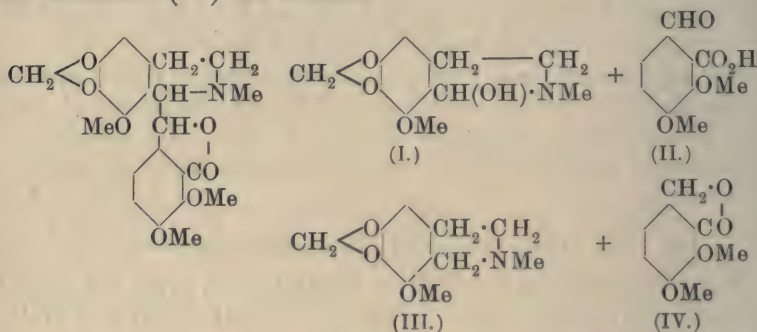
The azo-compound formed by coupling the quinonediazide with β -naphthol is characterised by being non-crystalline, a somewhat exceptional property among azo-derivatives of β -naphthol. For this reason, and owing to the circumstance that we had only a very small quantity of the substance at our disposal, the compound has only been examined qualitatively. It is distinctly more soluble in alcohol and acetic acid than its isomeride; its solutions are red, and it separates from a hot saturated solution in glacial acetic acid in reddish-brown, amorphous nodules. It is distinctly phenolic, dissolving in dilute alkali with a violet colour, and forming a sodium salt, which is easily "salted out" by excess of sodium hydroxide or by more soluble salts. The sodium salt is also amorphous. The melting point of the compound obtained by deposition from acetic acid and washing with alcohol is about 197° . It dissolves in concentrated sulphuric acid with a fine blue colour, becoming violet on dilution with water.

We have great pleasure in acknowledging the co-operation of Mr. Harold Kuntzen in carrying out the experimental part of this investigation.

CVI.—*Synthesis of Cotarnine.*

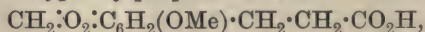
By ARTHUR HENRY SALWAY.

THE alkaloid narcotine, as is well known, is converted by oxidising agents into cotarnine (I) and opianic acid (II), but when the degradation is effected by reducing agents, hydrocotarnine (III) and meconine (IV) are obtained:



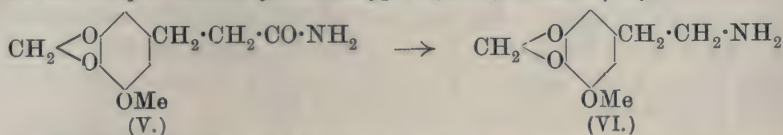
It is therefore evident that the problem of the complete synthesis of narcotine depends for its solution on the following three factors: (1) the synthesis of the degradation products, cotarnine or hydrocotarnine, and opianic acid or meconine; (2) the recombination of these substances to form racemic narcotine; and (3) the resolution of the latter into its enantiomorphous components. The first step in this direction was the synthesis of meconine from guaiacol, which was accomplished by Fritsch (*Annalen*, 1898, **301**, 351), whilst Perkin and Robinson (*Proc.*, 1910, **26**, 46 and 131) have not only succeeded in recombining cotarnine and meconine with the production of *dl*-narcotine, but have also resolved the latter into its optically active components. In order, therefore, to complete the synthesis of the natural alkaloid, the synthesis of cotarnine alone remained to be accomplished. The present author has for some time been engaged on this task, which has now been brought to a successful conclusion.

The steps by which the synthesis of cotarnine has now been attained may be briefly described as follows. Myristicin, $\text{CH}_2\text{:O}_2\text{:C}_6\text{H}_2(\text{OMe})\text{:CH}_2\text{:CH:CH}_2$ (compare Power and Salway, *Trans.*, 1907, **91**, 2054), was first converted into β -3-methoxy-4:5-methylenedioxyphenylpropionic acid,

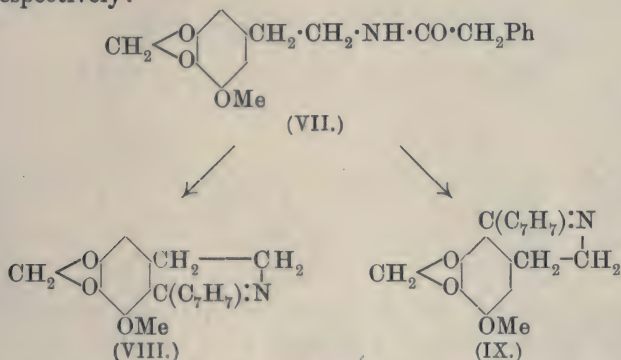


by a series of reactions which has previously been described (*Trans.*, 1909, **95**, 1204). This acid was next transformed into its *amide*

(V), and the latter converted by means of Hofmann's reaction into β -3-methoxy-4: 5-methylenedioxyphenylethylamine (VI):



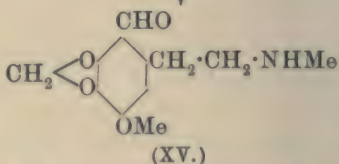
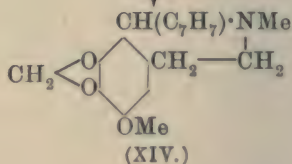
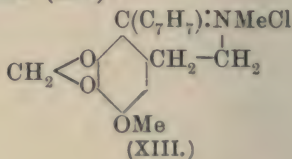
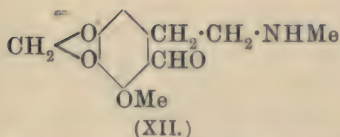
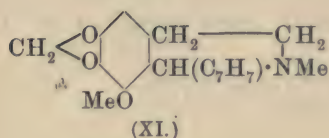
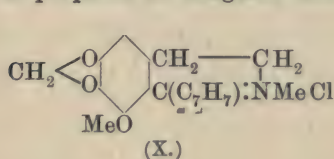
The *phenylacetyl* derivative of this base (VII) was then condensed by heating with phosphoric oxide in the presence of xylene, according to a method similar to that employed by Pictet and Finkelstein (*Ber.*, 1909, **42**, 1979) in the synthesis of laudanosine. In this condensation it is evident that theoretically two isomeric dihydroisoquinoline derivatives (VIII and IX) may be formed. Both of these isomeric compounds have, in fact, been isolated in the form of their hydrochlorides, which decompose at 192° and 174° respectively:



It has, furthermore, been possible to assign to the above-mentioned isomerides their respective formulæ (VIII and IX), since the compound decomposing at 192° , when treated as indicated below, yielded cotarnine, and must therefore be represented by (VIII), whilst the substance decomposing at 174° gave an isomeride of cotarnine, and consequently possesses the formula (IX).

For the preparation of cotarnine from 8-methoxy-6: 7-methylenedioxy-1-benzyl-3: 4-dihydroisoquinoline (VIII), the latter was first converted into its methochloride (X), and this reduced with tin and hydrochloric acid. The product, 1-benzylhydrocotarnine (XI), was then oxidised by manganese dioxide in the presence of sulphuric acid (compare Pyman, *Trans.*, 1909, **95**, 1751), when it yielded a substance which was identical in all respects with cotarnine (XII). The identity was established by means of analyses and by a comparison of its derivatives with the corresponding derivatives of a specimen of cotarnine which had been obtained by the oxidation of narcotine.

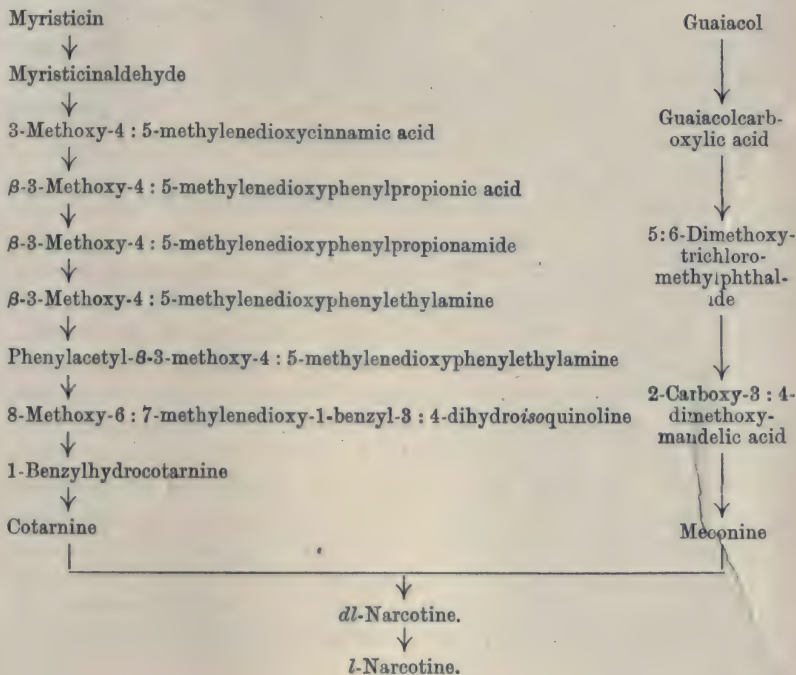
The hydrochloride of 6-methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline (IX) was also converted into its methochloride (XIII), and then reduced to 6-methoxy-7:8-methylene-dioxy-1-benzyl-2-methyl-1:2:3:4-tetrahydroisoquinoline (XIV). The latter, when oxidised, gave an isomeride of cotarnine, which it is proposed to designate *neocotarnine* (XV):



A comparison of the characters of synthetic cotarnine, *neo*-cotarnine, and the cotarnine obtained from narcotine, and of their respective derivatives, is presented in the following table:

	Free base.	Hydrochloride.	Aurichloride.	Picrate.
1. Synthetic cotarnine.	Colourless needles, decompose at 130°	Colourless needles, decompose at 197°	Golden-yellow plates, melt at 136—137°	Yellow needles, melt at 143°
2. Cotarnine from narcotine.	Colourless needles, decompose at 131°	" "	" "	" "
3. Mixture of synthetic cotarnine with cotarnine from narcotine.	Decompose at 129°	" "	" "	" "
4. <i>neo</i> Cotarnine.	Colourless prisms, decompose at 124°	Yellow or red needles (two modifications), decompose at 185°	Chocolate-brown prisms, melt at 127°	Yellow needles, sinter at 90°, melt at 100°

The synthesis of cotarnine having now been accomplished, that of the alkaloid narcotine has become complete. The stages by which these syntheses have been effected may be represented by the following scheme:



EXPERIMENTAL.

β -3-Methoxy-4 : 5-methylenedioxyphenylpropionamide (V, p. 1209).

For the preparation of this compound, 100 grams of β -3-methoxy-4 : 5-methylenedioxyphenylpropionic acid,* which had been obtained from myristicin by a series of reactions described in a previous investigation (Trans., 1909, **95**, 1208—1210), were dissolved in benzene, and the solution gently warmed with 1 molecule of phosphorus pentachloride until the reaction was complete. The mixture was then heated on the water-bath under diminished pressure for some time, whereby the solvent, and the phosphoryl chloride which had been formed, were completely removed. The residual crude acid chloride, dissolved in benzene, was gradually added, with vigorous agitation, to an excess of concentrated aqueous ammonia. The

* The melting point of β -3-methoxy-4 : 5-methylenedioxyphenylpropionic acid was erroneously given as 124—125° in the previous paper (*loc. cit.*). The correct melting point of this compound is 99—100°.

precipitate of acid amide thus formed was collected and recrystallised from alcohol, when it separated in long, colourless needles, melting at 129—130°:

0.1246 gave 0.2706 CO₂ and 0.0672 H₂O. C=59.2; H=6.0.

C₁₁H₁₃O₄N requires C=59.2; H=5.8 per cent.

β-3-Methoxy-4: 5-methylenedioxyphenylpropionamide is readily soluble in chloroform or alcohol, but only sparingly so in ether or benzene. It may be crystallised from hot benzene, and separates from this solvent in well-formed, colourless needles.

β-3-Methoxy-4: 5-methylenedioxyphenylethylamine (VI, p. 1209).

Ninty grams of finely powdered *β*-3-methoxy-4: 5-methylenedioxyphenylpropionamide were added to 1400 c.c. of an alkaline solution of sodium hypochlorite containing 77 grams of active chlorine (compare Graebe, *Ber.*, 1902, **35**, 2753), and the mixture was shaken continuously until the amide had completely dissolved, for which about two hours were necessary. The clear solution was then heated for a short time (fifteen minutes) on the boiling-water bath, when a dark-coloured oil separated, which was extracted with ether. The ethereal solution was washed with water, and subsequently shaken with dilute hydrochloric acid until the base was completely extracted. A small portion of this acid solution, when concentrated to a small volume, yielded a crystalline *hydrochloride*, which was purified by recrystallisation from a mixture of absolute alcohol and ethyl acetate. It separated from this solvent in colourless needles, melting at 165°:

0.1496 gave 0.2826 CO₂ and 0.0850 H₂O. C=51.5; H=6.3.

C₁₀H₁₄O₃NCl requires C=51.8; H=6.0 per cent.

β-3-Methoxy-4: 5-methylenedioxyphenylethylamine, as obtained from its hydrochloride, was a light brown oil, which did not solidify on keeping. Its *benzoyl* derivative crystallises from a mixture of benzene and light petroleum in shining, colourless, flat prisms, melting at 90—91°.

Phenylacetyl-β-3-methoxy-4: 5-methylenedioxyphenylethylamine (VII, p. 1209).

The solution of *β*-3-methoxy-4: 5-methylenedioxyphenylethylamine hydrochloride obtained in the above reaction was directly converted into the phenylacetyl derivative by shaking with an excess of phenylacetyl chloride in the presence of alkali. After a short time the desired compound separated as a light brown solid; this was collected, and crystallised from alcohol, from which it separated in well-formed, colourless needles, melting at 103—104°:

0.1206 gave 0.3066 CO_2 and 0.0669 H_2O . $\text{C}=69.3$; $\text{H}=6.2$.

$\text{C}_{18}\text{H}_{19}\text{O}_4\text{N}$ requires $\text{C}=69.0$; $\text{H}=6.1$ per cent.

Phenylacetyl- β -3-methoxy-4:5-methylenedioxyphenylethylamine is readily soluble in chloroform or alcohol, but only moderately so in water or cold benzene.

Condensation of Phenylacetyl β -3-Methoxy-4:5-methylenedioxyphenylethylamine.

The condensation of this substance to the corresponding dihydro-isoquinoline was conducted according to a method first proposed by Bischler and Napieralski, and recently modified by Pictet and Kay (*Ber.*, 1909, **42**, 1973). Sixty-five grams of phenylacetyl β -3-methoxy-4:5-methylenedioxyphenylethylamine were dissolved in 500 c.c. of xylene, and 100 grams of phosphoric oxide then added. After heating the mixture for about fifteen minutes a further 80 grams of phosphoric oxide were added, and the heating continued until a small portion of the xylene gave no precipitate of unchanged substance on the addition of light petroleum. The xylene was then decanted from the yellow mass of phosphorus compound, and the latter extracted with hot water until only an insoluble resin remained undissolved. The aqueous extract was shaken with ether to remove adhering xylene, then rendered alkaline with sodium hydroxide, and the oil, which was thus precipitated, extracted with ether. After the ethereal solution had been washed, dried, and the solvent removed, there remained a viscid, brown oil, which did not solidify, and amounted to 40 grams.

Separation of Two Isomeric Methoxymethylenedioxybenzylidihydro-isoquinolines (VIII and IX, p. 1209).

Since the condensation of phenylacetyl β -3-methoxy-4:5-methylenedioxyphenylethylamine can proceed in two directions, it was to be expected that the above brown, oily condensation product would consist of a mixture of two isomeric bases. In order to effect a separation of these compounds, the oil was dissolved in dry ether and a current of dry hydrogen chloride passed into the solution, when the hydrochlorides were precipitated as a light brown solid. This mixture of crude hydrochlorides was then fractionally crystallised from a mixture of absolute alcohol and ethyl acetate. After considerable fractionation, two distinct hydrochlorides were isolated, one of which crystallised in colourless prisms, melting and decomposing at 192° , whilst the other separated in pale yellow, slender needles, which melted and decomposed at 174° . These compounds were analysed:

Substance melting and decomposing at 192°.

0.1020 * gave 0.2427 CO₂ and 0.0505 H₂O. C=64.9; H=5.5.

0.5061 * „ 0.2181 AgCl. Cl=10.7.

C₁₈H₁₈O₃NCl requires C=65.2; H=5.4; Cl=10.7 per cent.

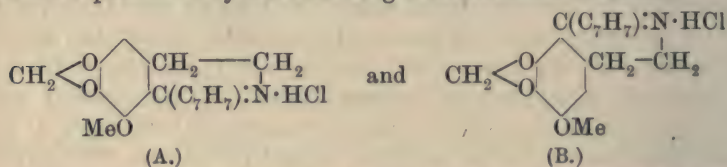
Substance melting and decomposing at 174°.

0.0936 * gave 0.2220 CO₂ and 0.0475 H₂O. C=64.7; H=5.6.

0.3986 * „ 0.1707 AgCl. Cl=10.6.

C₁₈H₁₈O₃NCl requires C=65.2; H=5.4; Cl=10.7 per cent.

From a consideration of these results, and the method of preparation of the two compounds, it is evident that they are isomeric and are represented by the following constitutional formulæ:



It has been possible to assign to the above-mentioned hydrochlorides their respective constitutional formulæ, since a substance of formula (A), on successive methylation, reduction, and oxidation, will yield cotarnine, whilst a compound having the formula (B) will yield, under similar treatment, an isomeride of cotarnine. The hydrochloride melting and decomposing at 192°, when subjected to the series of operations described below, has been found to give cotarnine, and must therefore possess the formula (A). It consequently follows that the hydrochloride melting and decomposing at 174° is represented by formula (B).

8-Methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline hydrochloride (A), when crystallised from a mixture of absolute alcohol and ethyl acetate, forms colourless prisms, which are anhydrous and possess an intensely bitter taste. It is very soluble in alcohol or water, and crystallises from a concentrated aqueous solution in pale yellow leaflets, containing two molecules of water of crystallisation. When the hydrated salt is heated it partly melts at 85° with loss of water of crystallisation and becomes colourless, whilst the anhydrous substance then melts and decomposes at 192° with the formation of a deep red liquid:

0.7074 lost at 100° 0.0686 H₂O. H₂O=9.7.

C₁₈H₁₈O₃NCl, 2H₂O requires H₂O=9.8 per cent.

The free base, 8-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline, as obtained from its hydrochloride by the addi-

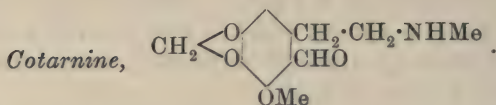
* Dried at 110°.

tion of sodium carbonate, is a viscid, colourless oil, which does not solidify. It yields a *picrate*, which is only sparingly soluble in hot water, but readily so in alcohol, from which it separates in glistening, yellow laminae, melting at 154°.

6-Methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline hydrochloride (B) crystallises from a mixture of absolute alcohol and ethyl acetate in pale yellow needles, which melt and decompose at 174°. It is readily soluble in alcohol or water, and from the latter it separates in long needles of a deep yellow colour. Unlike its isomeride, it does not possess a bitter taste. The free base, 6-methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline, is precipitated from a solution of the hydrochloride as a pale yellow, viscid oil, which does not solidify. The *picrate* crystallises from water, in which it is only sparingly soluble, in small, yellow needles, melting at 204°.

Methylation and Reduction of 8-Methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline.

The base regenerated from 7 grams of 8-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline hydrochloride was dissolved in methyl alcohol, an excess of methyl iodide added, and the mixture heated at 100° for an hour in a sealed tube. The methyl alcohol and excess of methyl iodide were removed by distillation, the residual crude methiodide dissolved in warm water, and then converted into the methochloride by shaking the solution for a short time with freshly precipitated silver chloride. After removing the silver chloride and iodide, the deep yellow filtrate was concentrated to dryness under diminished pressure, when the crude 8-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydroisoquinoline methochloride was obtained as a reddish-yellow, gummy mass. Without further examination, the latter was reduced by heating for forty-eight hours with tin and concentrated hydrochloric acid in the presence of alcohol. The hot liquid was then decanted from undissolved tin, water added, and the double salt of tin, which was precipitated, collected and decomposed by heating with aqueous sodium hydroxide. The base thus liberated was extracted with ether, the ethereal solution being washed, dried, and the solvent removed, when a brown, viscid oil was obtained. From the above method of preparation, this product should consist of 1-benzylhydrocotarnine, which has already been described by Freund and Reitz (*Ber.*, 1906, **39**, 2231) as a colourless, crystalline solid, melting at 70°. The synthetic product, however, did not solidify on keeping, and as the quantity of material was not large, it was deemed advisable to proceed to the final stage of the synthesis without its further purification.



The crude 1-benzylhydrocotarnine, amounting to 5.2 grams, was accordingly dissolved in 50 c.c. of a 10 per cent. aqueous solution of sulphuric acid, and oxidised (compare Pyman, *Trans.*, 1909, **95**, 1751) by heating for a short time on the boiling-water bath with 4 grams of pyrolusite (81 per cent. MnO_2). After cooling the mixture, it was extracted with benzene, which removed the non-basic oxidation product, consisting chiefly of benzaldehyde, and then rendered alkaline by means of sodium carbonate. The manganese carbonate thus precipitated was removed by filtration, and the filtrate first shaken with benzene, which extracted only a very small amount of basic substance, after which it was made strongly alkaline with sodium hydroxide, and the liberated base taken up in benzene. This benzene extract was washed with a little water and then shaken with small quantities of dilute hydrochloric acid until the basic substance was completely removed. On evaporating the acid liquid, a yellow, crystalline solid, amounting to 1.1 grams, was obtained, which was purified by recrystallisation from a mixture of absolute alcohol and ethyl acetate. It separated from this solvent in long, colourless needles, melting and decomposing at about 197° with the formation of a deep red liquid. On comparing this compound with a specimen of cotarnine hydrochloride prepared from the naturally-occurring alkaloid narcotine, the two were found to be identical in every respect:

0.3267,* on heating at 110° , lost 0.0378 H_2O . $\text{H}_2\text{O}=11.6$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}\cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=12.35$ per cent.

0.1162 † gave 0.2396 CO_2 and 0.0598 H_2O . $\text{C}=56.2$; $\text{H}=5.7$.

0.3075 † „ 0.1742 AgCl . $\text{Cl}=14.0$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}$ requires $\text{C}=56.4$; $\text{H}=5.5$; $\text{Cl}=13.9$ per cent.

Additional evidence of the identity of the synthetic cotarnine with that obtained from narcotine was afforded by a comparison of the respective aurichlorides and picrates, which do not appear to have hitherto been described.

Cotarnine Aurichloride.—This compound was first prepared from a specimen of cotarnine hydrochloride as derived from narcotine, when it was obtained as a voluminous, reddish-yellow precipitate, which was very sparingly soluble in water, but readily so in hot alcohol. It crystallised from the latter in golden-yellow laminæ, which melted at 136 — 137° , and were anhydrous. The aurichloride

* Air-dried.

† Dried at 110° .

from the above-described synthetic cotarnine hydrochloride also crystallised from alcóhol in golden-yellow laminae, melting at $136-137^{\circ}$, and the melting point of a mixture of the two specimens was the same. The synthetic aurichloride was ignited, with the following result:

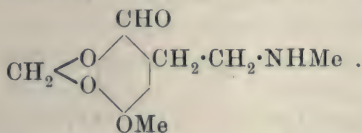
0.1342 gave 0.0475 Au. $\text{Au} = 35.4$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}_4\text{Au}$ requires $\text{Au} = 35.3$ per cent.

Cotarnine Picrate.—When aqueous picric acid is added to a solution of cotarnine hydrochloride, an oily precipitate is formed, which soon becomes solid. It is moderately soluble in hot water, from which it crystallises in slender, yellow, silky needles. These sinter at 133° , and melt at 143° . The picrate from the synthetic hydrochloride was prepared in a similar manner, and found to possess the same properties. The melting point of a mixture of the two specimens was 143° .

The identification of the above-described synthetic product was finally completed by the preparation of the free base itself, which was obtained as a colourless, crystalline solid when an aqueous solution of sodium hydroxide was cautiously added to a solution of synthetic cotarnine hydrochloride. The base was purified by recrystallisation from benzene, when it was deposited in stellar clusters of prismatic needles, which melted and decomposed at 130° . It was identical in all respects with a specimen of cotarnine prepared from narcotine.

neCotarnine, an Isomeride of Cotarnine,



For the synthesis of this substance, 6-methoxy-7:8-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline hydrochloride (B) (p. 1214) was subjected to the same series of operations as those which have already been described in connexion with the conversion of 8-methoxy-6:7-methylenedioxy-1-benzyl-3:4-dihydro*iso*quinoline into cotarnine. Accordingly, the base regenerated from 3 grams of the pure hydrochloride was successively converted into its methiodide and methochloride, and the latter reduced with tin and hydrochloric acid in the presence of alcohol. The reduction product, 1-benzyl*ne*cotarnine (XIV, p. 1210), was obtained as a brown oil, which was not further investigated, but directly oxidised by means of manganese dioxide and sulphuric acid. On examining the products of oxidation, a crystalline hydrochloride was isolated,

which was purified by crystallisation from a mixture of absolute alcohol and ethyl acetate. It separated from this solvent in long, bright yellow needles, which melted and decomposed at 185° with the formation of a deep red liquid:

0.1486 * gave 0.3070 CO_2 and 0.0782 H_2O . $\text{C}=56.3$; $\text{H}=5.8$.

0.2968 * „ 0.1620 AgCl . $\text{Cl}=13.5$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}$ requires $\text{C}=56.4$; $\text{H}=5.5$; $\text{Cl}=13.9$ per cent.

Since a mixture of the above substance and cotarnine hydrochloride decomposes at about 170° , the two cannot be identical, and must therefore be isomeric. It is proposed to designate the new base *neocotarnine*.

neocotarnine hydrochloride is readily soluble in water or alcohol, but insoluble in ether or ethyl acetate. It is best crystallised from a mixture of absolute alcohol and ethyl acetate, from which it separates in long, yellow needles containing $1\frac{1}{2}$ molecules of water of crystallisation:

0.4665, when heated at 110° , lost 0.0438 H_2O . $\text{H}_2\text{O}=9.4$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=9.6$ per cent.

In losing its water of crystallisation, the bright yellow hydrochloride changes in colour to dark red. This change is not due to decomposition, since, on the one hand, the red hydrochloride re-absorbs $1\frac{1}{2}$ molecules of water and becomes yellow again on exposure to air, whilst, on the other hand, the yellow hydrochloride, when dried in a vacuum over sulphuric acid, loses its water of crystallisation without any change of colour. The yellow, anhydrous substance so obtained then becomes red, without loss in weight, by prolonged heating at 110° :

0.3538 anhydrous substance absorbed 0.0378 H_2O on exposure to air. $\text{H}_2\text{O}=9.7$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}, 1\frac{1}{2}\text{H}_2\text{O}$ requires $\text{H}_2\text{O}=9.6$ per cent.

neocotarnine.—The free base differs from its isomeride, cotarnine, in not being precipitated from an aqueous solution of its hydrochloride by the addition of dilute alkali hydroxides. It may, however, be obtained from such an alkaline solution by extracting with benzene and removing the solvent in a vacuum. The base then remains as a hard, crystalline mass, which, on recrystallisation from benzene, is deposited in colourless prisms, melting and decomposing at 124° .

neocotarnine is readily soluble in alcohol, chloroform, or ethyl acetate, but only sparingly soluble in ether. It dissolves in hot water, giving a yellow solution, from which it does not readily separate. The *aurichloride* is precipitated as a dark brown solid

* Dried at 110° .

on the addition of gold chloride to an aqueous solution of *neocotarnine* hydrochloride. It is only sparingly soluble in water, but readily so in hot methyl alcohol, from which it crystallises in chocolate-brown prisms. These are anhydrous, and melt and decompose at 127°:

0.1398 gave 0.0489 Au. $\text{Au} = 35.0$.

$\text{C}_{12}\text{H}_{14}\text{O}_3\text{NCl}_4\text{Au}$ requires $\text{Au} = 35.3$ per cent.

neocotarnine picrate is obtained as an oily precipitate, which soon solidifies, when an aqueous solution of picric acid is added to *neocotarnine* hydrochloride. It is readily soluble in alcohol, but only moderately so in hot water, from which it is deposited in long, yellow needles, sintering at 90° and melting at 100°.

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LONDON, E.C.

CVII.—*The Direct Union of Carbon and Hydrogen.* *Synthesis of Methane. Part II.*

By WILLIAM ARTHUR BONE and HUBERT FRANK COWARD.

IN our previous paper on this subject (Trans., 1908, **93**, 1975), experiments were described in which 73 per cent. of the theoretical yield of methane was obtained by heating less than 0.1 gram of highly purified sugar charcoal to a temperature of about 1150° in a current of pure and thoroughly dried hydrogen, thus establishing beyond all doubt the direct synthesis of methane as originally reported by Bone and Jerdan in 1897 (Trans., **71**, 41), the validity of which had been questioned by Berthelot (*Compt rend.*, 1905, **40**, 905; *Ann. Chim. Phys.*, 1905, [viii], **6**, 183), by Pring and Hutton (Trans., 1906, **89**, 1591), and also by Mayer and Altmayer (*Ber.*, 1907, **40**, 2134).*

Our failure to achieve an absolutely quantitative conversion of carbon into methane was ascribed to the reducing action of the gas on the inner surface of the porcelain tube used in the experiments referred to, and in a footnote (*loc. cit.*, p. 1988) it was reported that, subsequent to the writing of the paper, Dr. Ernest Feilmann had, as a result of a careful microchemical analysis, discovered unmistakable signs of lead in the glaze of the porcelain tube, a circumstance which would sufficiently explain the partial loss of methane during the experiments.

* We may refer the reader to pp. 1976—1978 of our previous paper (*loc. cit.*) for a detailed criticism of the inconclusive experiments of all these authors.

Correspondence was at once entered into with the authorities of the Royal Berlin Factory, where the porcelain tubes had been manufactured, and as the result of a careful inquiry we were informed that whereas "die Glasure, welche für unser Hartporzellan verwendet wird, vollkommen bleifrei ist," the batch of tubes in question had been fired in a kiln which had been accidentally fouled by certain lead glazes and enamels. The factory authorities very kindly undertook specially to prepare a new batch of tubes for our further experiments; these were carefully tested for us by Dr. Feilmann, and although he was unable to report their absolute freedom from lead, the amount of contamination was very much smaller than in the tubes previously used. On repeating our experiments with these new tubes, we have succeeded in obtaining as nearly as possible quantitative yields of methane (certainly exceeding 95 per cent.) from less than 0.03 gram of highly purified carbon.

Before describing these further experiments, however, we desire to refer to certain points raised in Mr. Pring's recent paper on this subject (this vol., p. 498). It is satisfactory to note that this author, now that he has adopted the method for estimating small percentages of methane previously devised by us, acknowledges the probability (p. 500) "that the conclusions of Bone and Jerdan and Bone and Coward, that carbon unites directly with hydrogen to form methane, will be upheld," but later on (p. 503) he quite unjustifiably casts an aspersion on the method employed by us, in common with Bone and Jerdan, for purifying the carbon. Thus, he remarks, "The method . . . for purifying the carbon consisted in igniting the finely divided substance for several days in a stream of chlorine, followed by hydrogen, at a temperature of 1100—1200°. The disadvantage of this method lies in the improbability of ever being able to remove the last traces of combined hydrogen, and the serious contamination which must result from contact with the containing vessel during the long period necessary for the treatment."

In our previous paper analyses of the carbon purified according to our method were given (*loc. cit.*, p. 198), showing that it contained no more than 0.06 per cent. of hydrogen, of which at least part was undoubtedly present in an "occluded" form. We are also happily in a position to refute Mr. Pring's unwarranted suggestion of "serious contamination" from contact with the walls of the containing vessel, seeing that the ash content of our purified carbon has never exceeded 0.06 per cent. As Mr. Pring states in his last paper (p. 504) that his highly purified rods contained "less than 0.10 per cent. of hydrogen and 0.05 per cent. of ash," he is

not entitled to infer that he used a purer form of carbon than previous workers.

Shortly after the appearance of our previous paper, E. I. Orloff (*J. Russ. Phys. Chem. Soc.*, 1908, **40**, 1588) claimed to have synthesised ethylene by passing a mixture of approximately equal volumes of carbon monoxide and hydrogen over pieces of coke impregnated with reduced nickel and palladium, and maintained at 95° to 100° only. The exit gas, he said, contained in one experiment 6.6, and in another 8.3 per cent. of "ethylene," which, however, *could not be absorbed by means of either bromine or bromine water*, although it was rapidly taken up by a concentrated solution of potassium mercuric iodide in sodium hydroxide. This supposed synthesis of ethylene was also quoted with approval in the "Annual Reports" for 1909 (p. 77). According to our experience, however, whereas ethylene, diluted with carbon monoxide and hydrogen in the proportion reported by Orloff, is rapidly and completely absorbed by bromine, it is practically untouched by the reagent employed by him for its removal.

EXPERIMENTAL.

The apparatus and experimental procedure adopted by us in the following experiments was in all important respects identical with that already described in detail in our previous paper (pp. 1982 to 1992), with the exception that the arrangement of two coaxial tubes containing the carbon was heated electrically instead of in a gas furnace. In each of the three following experiments we succeeded in almost quantitatively converting about 0.03 gram of highly purified sugar charcoal into methane by maintaining it at about 1150° in a steady current of thoroughly dried hydrogen prepared by the electrolysis of a solution of recrystallised barium hydroxide. The rate of flow of the gas through the heated tube was about 1000 to 1100 c.c. per hour, and each experiment extended over an unbroken period of from seventeen to twenty-five hours. In order to accelerate the methane formation, and thus complete each experiment within a period which would not overtax either the capability of the apparatus for withstanding the fierce temperature, or the physical endurance of the operators, the purified carbon was previously intimately mixed with about 4 per cent. of its weight of finely divided platinum.

At the outset of each experiment a weighed quantity of the carbon was introduced into the inner of the two coaxial porcelain tubes, which in all but one experiment was protected by a loose quartz lining; the carbon was not (as in some of our previous experiments) contained in a platinum boat, but was in immediate

contact with either the porcelain tube or its quartz lining. As soon as all the air in the apparatus and its connexions had been thoroughly displaced by dry hydrogen, the coaxial porcelain tubes were as rapidly as possible raised to the experimental temperature, the current of hydrogen being suspended until the full heat of the furnace had been attained. After re-starting the current of hydrogen, the whole of the exit gas was collected, during several successive periods of about five hours each throughout the experiment, in a series of graduated glass holders over a mixture of equal volumes of water and glycerol.

At the end of each experiment the gas current was stopped, and after the porcelain tubes had cooled down to the room temperature, any small quantity of unchanged carbon remaining in the inner tube was carefully withdrawn and estimated, its weight being deducted from that of the carbon originally taken.

The gaseous contents of the various gas-holders, having attained the laboratory temperature, were measured, and a litre sample withdrawn from each for subsequent concentration over palladium foil to about 25 c.c., as described on p. 1979 of our previous paper. Each concentrate was finally carefully measured in a graduated burette over mercury, and thereafter submitted to an accurate analysis for oxides of carbon (if any), methane, and hydrogen. In this way a very accurate determination of the methane content of the gas collected during each successive period of the experiment was effected, and we regard the figures recorded for methane as significant to certainly the second, and possibly even the third, decimal place.

There was never any carbon dioxide in the products, and very rarely any carbon monoxide; even when the latter could be detected, it rarely exceeded 0.01 per cent. in the gases issuing from the heated tube. The nitrogen content of these gases was usually well below 0.1 per cent.

Purification and Analysis of the Carbon Used.

The sugar charcoal employed had been previously purified by being heated (1) in a constantly maintained vacuum at 600° for twenty-four hours, (2) in dry chlorine at 1150° for twenty-four hours, followed by (3) in pure dry hydrogen at 1150° for forty-eight hours. Analysis showed that it contained not more than 0.06 per cent. of ash and less than 0.1 per cent. of hydrogen, mainly in an "occluded" form. Before being used in the experiments, it was intimately mixed with 4 per cent. of its weight of finely divided platinum.

Purity of the Hydrogen.—A litre of the hydrogen used was

collected in a holder over the mixture of equal parts of glycerol and water, and subsequently concentrated over palladium foil at 100° to 25.3 c.c. Analysis of this concentrate showed that the original gas had contained: Hydrogen = 99.98 ; methane = 0.007 ; and nitrogen = 0.013 per cent. This is probably an exaggerated estimate of the hydrocarbon impurity present, and must be considered as a *maximum* figure.

Experiment I.

November 28-29th, 1908. Temperature = 1150° .

The inner porcelain tube was fitted with a quartz lining.

Carbon taken (after allowing for 4 per cent. of platinum added)... 0.0327 gram
Carbon remaining over at the end of the experiment 0.0028 ,,

Carbon used 0.0299 ,,

Methane corresponding with 0.0299 gram carbon = 55.8 c.c. at 0° and 760 mm.

Total duration = $17\frac{1}{2}$ hours. Total hydrogen used = 18 litres at 0° and 760 mm.

Period	1	2	3	4	5
Time (hours)	0—5½	5½—10½	10½—11½	11½—16½	16½—17½
Total volume of gas collected (litres)	5.6	5.6	1.0	5.7	1.0
Pressure (mm.)	769	772	—	775	775
Temperature	12°	12°	—	13°	13°
Percentages in the gas collected	$\left\{ \begin{array}{l} \text{CO} \dots\dots 0.020 \\ \text{CH}_4 \dots\dots 0.505 \\ \text{N}_2 \dots\dots 0.140 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ 0.375 \\ 0.090 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ 0.180 \\ 0.030 \end{array} \right.$	$\left\{ \begin{array}{l} 0.02 \\ 0.085 \\ 0.090 \end{array} \right.$	$\left\{ \begin{array}{l} \text{nil} \\ 0.04 \\ 0.01 \end{array} \right.$

Total methane in the gas collected 54.72 c.c. at 0° and 760 mm.

Less 0.007 per cent. (*maximum*) of methane in the 18 litres of hydrogen used..... 1.26 ,, ,, ,,

Methane from carbon..... 53.46 ,, ,, ,,

The yield of methane in this experiment was, therefore, not less than 95.8 per cent. of that theoretically obtainable.

Experiment II.

December 3-4th, 1908. Temperature = 1150°.

No quartz lining was used in this experiment.

Carbon taken (after allowing for 4 per cent. of platinum added)... 0·0272 gram
 Carbon left at the end of the experiment..... 0·0033 „
 Carbon used 0·0239 „

Methane corresponding with 0·0239 gram carbon = 44·4 c.c. at 0° and 760 mm.

Total duration = 21½ hours. Total hydrogen used = 22·4 litres at 0° and 760 mm.

Period	1	2	3	4	5	6
Time (hours)	0—5½	5½—10½	10½—15½	15½—16½	16½—20½	20½—21½
Total volume of gas collected (litres)...	5·7	5·6	5·7	1·0	4·6	1·0
Pressure (mm.)	774	773	773	773	772	772
Temperature	12°	12°	12°	12°	14°	14°
Percentages in $\begin{cases} \text{CO} \\ \text{the gas} \\ \text{collected} \end{cases}$	0·030	nil	nil	nil	nil	0·01
$\begin{cases} \text{CH}_4 \\ \text{N}_2 \end{cases}$	0·305	0·230	0·165	0·115	0·095	0·06
	0·030	0·050	0·030	0·020	0·090	0·20

Total methane in the gas collected 44·00 c.c. at 0° and 760 mm.

Less 0·007 per cent. (*maximum*) of methane
 in the 22·4 litres of hydrogen used..... 1·57 „ „ „

Methane from carbon..... 42·43 „ „ „

The yield of methane in this experiment was, therefore, not less than 95·6 per cent.
 of that theoretically obtainable.

Experiment III.

April 15-16th, 1909. Temperature = 1120—1150°.

The inner porcelain tube was fitted with a quartz lining.

Carbon taken (after allowing for 4 per cent. of platinum added)... 0.03283 gram

Carbon left at the end of the experiment..... 0.00420 „

Carbon used 0.02863 „

Methane corresponding with 0.02863 gram of carbon = 53.4 c.c. at 0° and 760 mm.

Total duration = 25 hours. Total hydrogen used = 28.35 litres at 0° and 760 mm.

Period	1	2	3	4	5	6	7
Time (hours)	0—5	5—9½	9½—14	14—18½	18½—19½	19½—24	24—25
Total volume of gas collected (litres)	5.75	5.75	5.75	5.60	1.00	5.60	1.00
Pressure (mm.) ...	766	764	760	762	762	763	763
Temperature	20°	20°	22°	22°	19°	21°	21°
Percentages { CO in the gas { CH ₄ collected { N ₂	nil 0.41 0.04	nil 0.275 0.050	0.010 0.125 0.070	0.010 0.070 0.040	0.010 0.050 0.090	nil 0.060 0.080	nil 0.03 0.12

Total methane in the gas collected 50.6 c.c. at 0° and 760 mm.

Less 0.007 per cent. (*maximum*) in the 28.35

litres of hydrogen used 2.0 „ „ „

Methane from carbon 48.6 „ „ „

The yield in this experiment was, therefore, approximately 91 per cent. of that theoretically obtainable.

In conclusion, we desire to express our indebtedness to Dr. Feilmann for his very skilful microchemical examinations of the porcelain tubes used in the above experiments, and also to the Government Grant Committee of the Royal Society for help in meeting part of the expense of the experiments.

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CVIII.—*The Interaction of Nickel Carbonyl and Carbon Disulphide.*

By SIR JAMES DEWAR and HUMPHREY OWEN JONES.

DURING the course of a number of preliminary experiments on the chemical reactions of nickel carbonyl, carried out in 1902, its reaction with carbon disulphide was examined. Equal volumes of nickel carbonyl and carbon disulphide were sealed up in an exhausted glass tube, and it was observed that, on keeping at the ordinary temperature of the laboratory, a very small quantity of a black powder was deposited from the liquid and a bronze mirror was formed on the tube in the vapour space above the liquid. On heating the tube to 100° , the bronze mirror was formed over its whole surface and pressure was developed, due to the liberation of carbon monoxide. Examination of the bronze-coloured deposit showed that it contained nickel and sulphur.

Conditions Affecting the Reaction.—In order to investigate this reaction further, the two liquids were introduced into a Lunge nitrometer over mercury, and the progress of the reaction was observed by measurement of the carbon monoxide evolved. When the mixture of liquids in different proportions, varying from 10 volumes of nickel carbonyl and 1 volume of carbon disulphide, to 1 volume of nickel carbonyl and 10 volumes of carbon disulphide, was kept in the nitrometer, we were surprised to find that quite an insignificant quantity of gas was evolved, only 0.2 to 1.5 c.c. after several days. At the same time there was only a very minute black deposit. The differences observed with different proportions of the liquids were very small, but still noteworthy; the mixtures containing the smaller proportions of nickel carbonyl gave larger quantities of gas than those containing more nickel carbonyl. The evolution of gas is such a sensitive indication of any decomposition that we must conclude either, that the reaction practically does not take place or, that the carbon monoxide is retained in considerable quantity by the liquid mixture.

In order to exclude this possibility, the mixed liquids were saturated with carbon monoxide separately and again when mixed; this, however, made no difference; the quantity of gas evolved did not exceed 0.5 c.c. for 2 c.c. of a mixture of equal volumes of the two liquids.

This proved conclusively that nickel carbonyl and carbon disulphide react to an insignificant extent in the liquid state. The observations made in the first instance suggested that the reaction

took place more readily in the gaseous state. Consequently, 2 c.c. of a mixture of equal volumes of the two liquids were introduced into a Lunge nitrometer and kept for a day; the pressure was then diminished by lowering the open limb so as to produce a vapour space filled with the saturated vapours. In a few minutes the surface of the glass in the space thus filled with vapour was covered with the bronze-coloured deposit, and after two hours 8 c.c. of gas (saturated with the two vapours) had been produced. This quantity of gas had increased to 10 c.c. in five hours, but afterwards did not appear to increase appreciably. The pressure was now still further diminished, the clean surface of the tube thus exposed became coated rapidly, and 24 c.c. of gas were formed in fifteen hours, and this quantity increased to 29 c.c. in twenty-four hours.

Experiments were then made in which the two liquids were introduced into a Lunge nitrometer, and a vapour space produced by the introduction of a gas, either pure dry hydrogen or nitrogen. Again the tube in the vapour space rapidly became coated with the bronze deposit, and the volume of gas increased, rapidly at first, and then more slowly until it remained constant for days.

The following example illustrates the changes observed.

8.4 c.c. of hydrogen were introduced above 2 c.c. of a mixture of equal volumes of the liquids, and immediately expanded to 16.2 c.c. In twenty-five seconds a black deposit was formed on the glass in the space occupied by gas, and

After	5 minutes	the volume of gas was	18.8 c.c.	
„	20 „	„	„	21.0 „
„	18 hours	„	„	24.0 „
„	3 days	„	„	24.0 „

Results of a similar kind were obtained with nitrogen. The vapour pressure of nickel carbonyl at 15° is 272 mm. (Dewar and Jones, *Proc. Roy. Soc.*, 1903, **71**, 435), and that of carbon disulphide at the same temperature is 244 mm., so that when the saturated vapours are mixed, the two constituents are present in approximately molecular proportions, nickel carbonyl being probably slightly in excess.

From the above experiments, it appears that nickel carbonyl and carbon disulphide do not interact to an appreciable extent in the liquid state, yet do so in the vapour state at the same temperature, and that the interaction is favoured by decrease of pressure. In this respect the reaction resembles the oxidation of phosphorus and of aldehyde vapour by dry oxygen, in both of which cases the reaction is favoured by decrease of pressure (Ewan, *Zeitsch. physikal. Chem.*, 1895, **16**, 315). It also appears that the

reaction comes to an end while both substances are still present, and is therefore an incomplete reaction.

In our previous experiments on the dissociation of nickel carbonyl (*loc. cit.*), it was shown that the stability of the molecule of nickel carbonyl was very greatly increased in the presence of carbon monoxide.

The presence of carbon monoxide also increases the stability of the nickel carbonyl molecule in the presence of carbon disulphide, and, if present in sufficient quantity, prevents the interaction of these two substances, as shown by the following experiment.

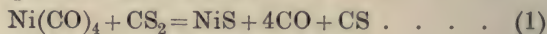
Carbon monoxide (10 c.c.) was introduced into a nitrometer, above 2 c.c. of a mixture of equal volumes of the liquids, and at once expanded to 15 c.c. After two days there was no visible deposit on the glass in the vapour space, and only a minute quantity of black powder had separated from the liquids; the volume of the gas was now 16 c.c.

Hence the presence of carbon monoxide appears to inhibit the reaction almost completely. On keeping such a mixture as that mentioned above for about two months, a thin bronze deposit was formed on the glass in the vapour space; consequently, a state of false equilibrium appears to be set up at first.

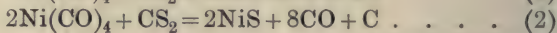
Course of the Reaction.—The bronze deposit forms a perfect mirror of great reflecting power even when thin enough to transmit light through it; in this respect it resembles the films of lead sulphide deposited on glass.

Examination of the properties of this bronze deposit indicated that it contained nickel sulphide, but it was found impossible to collect enough material for analysis when the two substances were allowed to interact in the cold. When the vapours were heated, even to 40° , from numerous analyses it was found that some metallic nickel was mixed with the deposit, which showed a varying composition, but usually contained a higher percentage of nickel than corresponded with nickel sulphide.

Assuming that carbon monoxide and nickel sulphide are two of the products of the reaction, then one of the following equations would probably represent the reaction:



or



If the first equation represents the reaction, carbon monosulphide might be found mixed with the carbon monoxide, or this substance might have polymerised and have been deposited with the nickel sulphide. Consequently, it was considered desirable to examine the gaseous product, and for this purpose the reaction was carried

out in the cold in a large glass globe,* or the vapours were passed through a long, spiral glass tube surrounded by warm water. The gaseous products were then passed through a series of three U-tubes, the first was surrounded by a freezing mixture, the second by liquid air, and the third by liquid air under exhaustion.* In this way all the gaseous products were liquefied, and the liquid was then fractionated.

Carbon monosulphide would be expected to boil at -130° , but in the liquefied products there was nothing boiling between the boiling point of nickel carbonyl and that of carbon monoxide. Hence, if carbon monosulphide is formed, it must have been deposited as a polymeride with the nickel sulphide.

The presence of carbon in the deposit was readily shown by heating some of the deposit in a stream of oxygen and passing the gases produced over lead chromate at a red heat.

In one experiment 0.4435 gram of the bronze deposit gave 0.0524 gram of carbon dioxide.

No quantitative relation could be established between the amount of nickel or sulphur and the amount of carbon in the deposit for the reason already stated, namely, that metallic nickel was always present. No evidence could be obtained, either by the action of heat or of concentrated sulphuric acid on the bronze deposit, of the presence of a substance having the properties of the polymeric form of carbon monosulphide already described (*Proc. Roy. Soc.*, 1910, A, 83, 526).

An attempt was then made to discriminate between the two suggested equations by measuring the volume of gas evolved when weighed quantities of the two substances were allowed to react.

Small weighed quantities (0.02 to 0.1 gram) of the two liquids were introduced into the graduated tube of a Hofmann vapour-density apparatus over mercury, the apparatus was kept at the ordinary temperature until no further increase in volume took place, and the volume of gas was then reduced to normal temperature and pressure. (The presence of either substance in excess would increase the apparent volume of the gas.) In this way the reaction took place mainly between the vapours, and there was no liquid visible at the end of the experiment.

The two following experiments may be given to illustrate the results obtained in this way.

(a) 0.0444 gram of nickel carbonyl and 0.0190 gram of carbon

* In this case, additional evidence was obtained showing that the reaction was incomplete. The vapours were allowed to remain until no further change took place, and it was found that both nickel carbonyl and carbon disulphide were present in the liquid obtained by cooling the contents of the bulb.

disulphide. Molecular proportions would be 0.0428 to 0.0190, and, on the basis of equation (1), 22.2 c.c. of gas should be evolved if carbon monosulphide is not among the gaseous products.

In two minutes 15.6 c.c. of gas were produced, and after two days 20.3 c.c.

The volume of gas is corrected to 0° and 760 mm., but no allowance has been made for the excess of nickel carbonyl. On heating a clean portion of the tube, a deposit was at once formed, showing that nickel carbonyl was still present.

(b) 0.094 gram of nickel carbonyl and 0.024 gram of carbon disulphide. Molecular proportions would be 0.054 gram to 0.024 gram; according to equation (1) 28.3 c.c. of carbon monoxide should be evolved, and according to equation (2) 48.8 c.c.

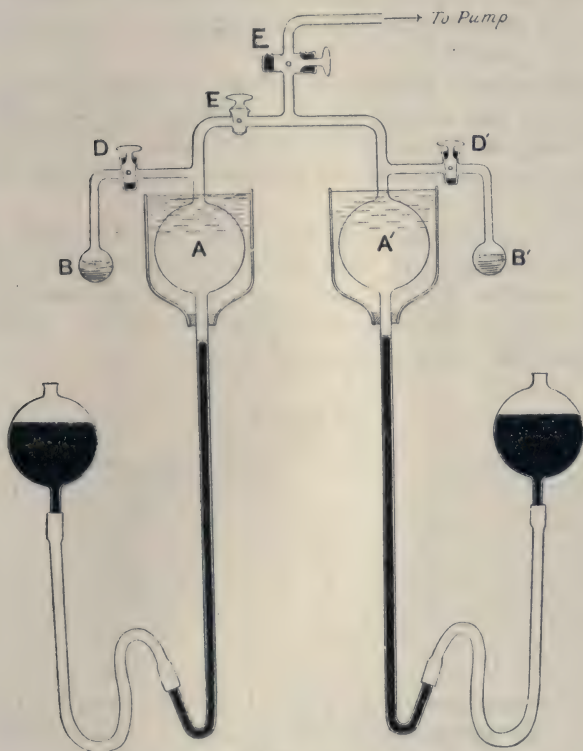
The final volume of gas obtained was 29.1 c.c. corrected to 0° and 760 mm., no allowance being made for the excess of nickel carbonyl if the reaction follows equation (1).

Considering that in experiment (b) there is an excess of nickel carbonyl over the amount required by equation (1), and an excess of carbon disulphide over that required by equation (2), the fact that the gas obtained, if corrected for the volume occupied by the excess of nickel carbonyl, is less than that required by equation (1), and, further, that nickel carbonyl was still present at the end of the experiment, it would appear that equation (1) represents the reaction rather than equation (2), but, on account of the incompleteness of the reaction, these experiments are inconclusive.

In order, first, to see whether more satisfactory results could be obtained by using definite quantities of the vapours at low pressures, when the reaction might be expected to proceed further, and, secondly, to investigate more fully the influence of carbon monoxide on the reaction, a special apparatus was devised for mixing equal volumes of the vapours and measuring the pressure of the gaseous products.

This apparatus is figured in the diagram. *A* and *A'* are two bulbs of nearly equal volume (about 80 c.c.), connected through two stopcocks *D* and *D'* with mercury seals to two small bulbs *B* and *B'*, containing respectively nickel carbonyl and carbon disulphide, and by means of flexible tubing to two mercury reservoirs *C* and *C'*. The bulbs *A* and *A'* are connected together through a stopcock *E*, can be put in connexion with a pump or a gas reservoir by means of the stopcock *F*, and are surrounded by baths which can be kept at the same constant temperature. The whole apparatus was first thoroughly exhausted by means of a Töpler pump or by charcoal in liquid air, while *B* and *B'* were immersed in liquid air. The stopcocks *D*, *D'*, *E*, and *F* were then closed. *D* and *D'* were

then opened, and the two bulbs *A* and *A'* were filled with the two vapours to any required pressure. The quantity of each vapour was determined by measuring the pressure in each bulb by means of a cathetometer; for this purpose the upper surface of the mercury was always brought to the same mark on the descending glass stem of the bulb *A* or *A'* for measurement. Thus, the same volume of each vapour could be obtained at any desired pressure. The vapours were then mixed by opening the stopcock *E*, and partly expelling the vapour from one bulb into the other by raising the



mercury reservoir (in doing this, care was taken to avoid condensation of the vapour). The rate at which the reaction proceeds could then be observed, and the final volume of gas produced could be measured easily either by measuring the pressure while the gas fills both bulbs, or by collecting it in one of the two bulbs and then measuring its pressure. This apparatus was found to be very convenient for investigating the interaction of vapours which produce gases, and has been used in other series of experiments besides those now described.

In order to attempt to discriminate between the two equations suggested, a number of experiments were made with the vapours of the constituents mixed in the proportions required according to these equations.

The details of a few of the experiments which were made with the two vapours alone have been selected, and are given in table I. In the first two columns the pressures (in millimetres of mercury) of the nickel carbonyl and carbon disulphide vapours are given; in the third column is the expected final pressure calculated on the assumption that complete reaction has occurred according to the equation (1), and in the fourth column the same according to the equation (2) (p. 1228).

The last column contains the final pressures observed after sufficient time had elapsed for the reaction to be completed; this required from four to nine hours in most cases.

All the experiments were carried out at the ordinary laboratory temperature of 14–18°.

The pressures of nickel carbonyl and carbon disulphide given in all cases and referred to later are the pressures prevailing when each vapour occupies one bulb only, whilst the calculated final pressures and the observed final pressures are the values which prevail when the gases occupy both bulbs.

TABLE I.

Exp.	Pressure in		Final pressure.		
	Ni(CO) ₄	CS ₂	Calculated,	Calculated,	Observed,
	bulb, mm.	bulb, mm.	Eq. 1, mm.	Eq. 2, mm.	
1.	36	47·0	77·5	86·5	72
2.	148	150·0	297·0	334·0	240
3.	69	31·0	81·0	127·5	103
4.	104	58·5	140·0	211·0	163
5.	158	64·0	175·0	271·0	188

In all the experiments, of which 1 and 2 above are typical, in which the two constituents were present in approximately equimolecular proportions, the value of the final pressure observed was less than that to be expected on the basis of equation (1), and in all cases the relative difference between the observed and calculated pressures was greater the higher the initial pressures of the two vapours. These experiments do not discriminate between the two equations, and are inconclusive, like those carried out in the Hofmann tube.

Now, on the other hand, in all the experiments in which approximately two molecular proportions of nickel carbonyl were present to one of carbon disulphide, the final pressure was greater

than that calculated on the basis of equation (1), and less than that calculated on the basis of equation (2). As before, the relative differences observed were dependent on the total pressure.

It therefore appears that the reaction between nickel carbonyl and carbon disulphide vapours must be represented by equation (2).

One possible source of error might be suggested, namely, that nickel carbonyl, although apparently dissociating slowly to a slight extent at the ordinary temperature in glass vessels, might be caused to dissociate more rapidly in a vessel covered with a deposit of nickel sulphide. Several experiments made with nickel carbonyl at various pressures from 50 to 100 mm. showed that there was no appreciable increase of pressure after several hours.

Table II contains a few of the experiments selected as typical of those made with the object of investigating the inhibiting influence of carbon monoxide on the reaction. In the third column is given the pressure of carbon monoxide in each bulb.

TABLE II.

Exp.	Pressure in		Pressure of CO in each bulb, mm.	Final pressure.		
	Ni(CO) ₄ bulb, mm.	CS ₂ bulb, mm.		Calculated, Eq. 1, mm.	Calculated, Eq. 2, mm.	Observed, mm.
6.	58	50	88.0	192.0	214.5	142
7.	75	65	68.5	203.5	232.2	139
8.	33	25	28.0	82.0	98.0	71
9.	62	68	28.0	155.0	170.5	112

It will be seen from these experiments that the reaction is very sensitive to the presence of carbon monoxide. In all cases where the proportion of carbon monoxide was greater than that in experiment 7, the two vapours being under a pressure of 50 mm. or more, there was no observable change. That is, when, on mixing the contents of the two bulbs, the pressure of the constituents were 37.5 mm. of nickel carbonyl, 32.5 mm. of carbon disulphide, and 68.5 mm. of carbon monoxide, or approximately two molecular proportions of carbon monoxide to one of nickel carbonyl along with one of carbon disulphide, the reaction is apparently completely inhibited. When the constituents were present in the same relative proportions at a lower pressure, as in experiment 8, the reaction did proceed to a limited extent, and the same result was obtained by reducing the proportion of carbon monoxide as in experiment 9.

The influence of carbon monoxide in inhibiting the reaction was also demonstrated by making a series of experiments comparable with those previously described by the authors (*loc. cit.*, p. 437)

to illustrate the influence of carbon monoxide on the dissociation of nickel carbonyl alone.

Tubes containing a small bulb filled with carbon disulphide were filled at different pressures with a mixture of 90 per cent. carbon monoxide and 10 per cent. nickel carbonyl, sealed off, the bulb broken, and the tube heated until a deposit was formed. In all cases a deposit was formed at a lower temperature than that at which a deposit of nickel would have appeared if no carbon disulphide had been present. Two examples will illustrate the kind of difference observed.

Total pressure in mm.	Temperature at which Ni was deposited when no CS ₂ was present.	Temperature at which NiS was deposited when CS ₂ was present.
50	100°	63°
400	170	100

Influence of Moisture and of Light on the Reaction.

Careful experiments were made to determine whether the reaction was influenced by the presence of impurities and particularly of moisture, and whether it was dependent in any way on the incidence of light on the mixture.

The reaction seemed to proceed quite as readily with carefully purified carbon disulphide as with the ordinary laboratory specimens. Experiments were then made under conditions such that moisture was carefully excluded. Small bulbs containing the two liquids and phosphoric oxide were sealed off, and then sealed up in a glass tube also containing a quantity of phosphoric oxide, and the whole kept for about a fortnight. The small bulbs were then broken by shaking, when it was found that the reaction proceeded rapidly, and a bronze deposit of nickel sulphide was formed over the tube in a few minutes.

The vapours from the two liquids, carefully dried by contact with phosphoric oxide for fourteen days, were allowed to mix in a dry apparatus, and again a bronze mirror was formed rapidly. Further, this reaction proceeded just as rapidly when light was rigorously excluded as when the vapours were exposed to light; the course of the reaction in this case was observed by noting the increase of pressure in a manometer connected to the bulb in which the vapours were mixed, and which was carefully shielded from light.

The reaction between nickel carbonyl and carbon disulphide proceeds therefore in the absence of light and of moisture.

A mixture of the two liquids in equal volumes is, however, changed on exposure to light; a flocculent, dark-coloured precipitate is gradually produced. This change is probably due to the

formation of sulphur from the carbon disulphide under the influence of light and the interaction of this with nickel carbonyl.

Thermochemistry of the Reaction.

Three determinations of the heat of formation of nickel carbonyl have been recorded. Reicher determined its heat of combustion, and hence deduced the heat of formation of the liquid carbonyl from solid nickel and carbon monoxide to be 59.5 Cal. Mittasch (*Zeitsch. physikal. Chem.*, 1902, **40**, 1) determined the heat of formation directly and obtained the value 52 Cal. for the liquid; he also calculated the heat of formation of nickel carbonyl vapour from the values of the dissociation constant at different temperatures. The values obtained in this way varied from 23.1 Cal. to 32.4 Cal.

The molecular latent heat of vaporisation of nickel carbonyl was found by us to be 6.4 Cal; hence the heat of formation of the gaseous compound from the first two values given for the liquid by Reicher and Mittasch would be 53.1 Cal. and 45.6 Cal. respectively.

The values given by Thomsen for $[C,S_2]$ gaseous and $[Ni_4S_{aq}]$ are respectively -26.0 Cal. and 17.4 Cal.; hence, taking the lower of the two values obtained by direct determinations for $[Ni_4CO \text{ gas}]$, the reaction (2), p. 1228, would involve an absorption of 30.8 Cal., whereas, if we take the value 24.3 Cal., the approximate mean of the indirect determinations, the reaction is exothermic and involves an evolution of 11.8 Cal.

The direct determination of the heat of formation of nickel carbonyl by combustion or by measuring the actual thermal evolution in the reaction between carbon monoxide and solid nickel is difficult and subject to great experimental error; in the first case, it is a small quantity compared to the heat of combustion of four molecules of carbon monoxide, and in the second, the rise of temperature observed was small, and this may have been caused in part by absorption or occlusion by the nickel of the nickel carbonyl. The conditions under which the value is deduced from the influence of temperature on the equilibrium are more comparable with the conditions under which the vapour reacts with the vapour of carbon disulphide in the experiments described in this paper.

Suggested Explanation of the Reaction.

The fact that this reaction proceeds readily in the gaseous state, whereas, at the same temperature, it is scarcely perceptible in the liquid state, may be due to the fact that the energy content of the vapour mixture is considerably less than that of the liquid mixture.

Taking the values for the heats of formation of the various compounds mentioned above, the reaction would still be endothermic if it took place between the liquids, whereas the reaction between the gases is very possibly slightly exothermic. Further, the reaction is facilitated by diminution of pressure, since it involves considerable expansion owing to the formation of the relatively large volume of carbon monoxide.

These considerations are, however, not adequate to account for the fact that under the conditions of pressure of varying composition of the mixture prevailing in the experiments above described, the reaction is incomplete at the ordinary temperature, and apparently is completely inhibited by the presence of carbon monoxide in sufficient quantity. The latter fact will explain why the reaction is incomplete, since the carbon monoxide liberated during the course of the interaction exerts its inhibiting action on the further progress of the reaction.

An explanation of this inhibiting action of carbon monoxide must therefore be sought.

The only reactions which are known to be incomplete, having once started, are reversible. It is impossible that either of the reactions (1) or (2) on p. 1228 can be of this character.

All the above-mentioned facts, however, find a ready explanation on the basis of the following hypothesis.

The dissociation of nickel carbonyl into nickel and carbon monoxide is reversible at the ordinary temperature, and even at lower temperatures. It must therefore be assumed that the nickel set free by dissociation has a definite, if exceedingly small, concentration in equilibrium with carbon monoxide.

If now we assume that carbon disulphide reacts with this free (dissociated) nickel and not with undissociated nickel carbonyl, it is possible to account for the incompleteness of the reaction.

The dissociation of nickel carbonyl is, as we have shown previously, very sensitive to the presence of carbon monoxide, as may be seen from the equation for the equilibrium:

$$K = \frac{C_{\text{Ni}} C_{\text{CO}}^4}{C_{\text{Ni(CO)}_4}}$$

and the extent of the dissociation is therefore very much reduced by the presence of carbon monoxide even at comparatively small concentrations. The carbon disulphide would now react with dissociated nickel, and form with it a deposit of nickel sulphide, thus disturbing the equilibrium between nickel carbonyl, nickel, and carbon monoxide. The carbon monoxide concentration would continually increase, and the concentration of the free nickel would continually diminish, until, finally, the latter would be practically

zero, when the reaction would cease. A diminution of pressure would now disturb the equilibrium between nickel carbonyl and carbon monoxide, and the reaction would again proceed until the concentration of nickel was again practically reduced to zero.

The influence of reduction of pressure is well illustrated by the experiments made in the Lunge nitrometer, and by the experiments made with the two-bulb apparatus; in the latter the reaction proceeded to a very much greater extent at low pressures than at high pressures.

Again an increase of temperature causes an increase in the dissociation of nickel carbonyl, and hence a rise of temperature causes the reaction with carbon disulphide to proceed a stage further when it had come to a standstill at a lower temperature.

The formation of nickel sulphide from a mixture of nickel carbonyl, carbon monoxide, and carbon disulphide proceeds at an appreciable rate even at temperatures much lower than the ordinary and under very low pressures. In order to show this, tubes containing small bulbs filled with the two liquids were exhausted, sealed, cooled in liquid air, and then shaken to break the small bulbs. These tubes were then allowed to remain completely immersed in liquid air, solid carbon dioxide, or in an ordinary freezing mixture. At -180° no deposit was formed after standing for five days; at -80° a distinct deposit was formed after two days; and at -20° an extensive deposit was observed after about three hours.

Experiments with Sulphur and with other Sulphur Compounds.

Sulphur.—In a previous paper (Trans., 1904, 95, 211) it was shown that nickel carbonyl reacted with solution of sulphur in carbon disulphide or xylene, giving carbon monoxide and nickel sesquisulphide.

The interaction of these two substances was now further examined, and it was shown that the black solid was produced from nickel carbonyl and a solution of sulphur in xylene even when both had been dried by contact with phosphoric oxide for ten days. In order to see whether the vapour of sulphur would react with the vapour of nickel carbonyl, sulphur was heated quickly in an exhausted tube so as to produce an extensive deposit of "molecular" sulphur on the walls of the tube, and nickel carbonyl vapour was then introduced at various pressures. On standing, a black deposit was formed on the glass over the deposit of molecular sulphur, and to a less extent on the clean portions of the glass. Thus the vapours of sulphur and nickel carbonyl do interact.

This reaction is, however, of a different kind from that which

takes place with carbon disulphide, since the deposit was formed in a tube containing sulphur, and filled with a mixture of 90 per cent. carbon monoxide and 10 per cent. nickel carbonyl under a pressure of 200 mm. At the ordinary temperature an extensive deposit was formed in about twelve hours, whereas under the same conditions carbon disulphide would have produced no deposit at 70°. This difference between the interactions of nickel carbonyl with sulphur and with carbon disulphide is presumably due to the fact that the former results in the formation of nickel sesquisulphide, whilst the latter gives nickel sulphide.

Carbonyl Sulphide.—A mixture of carbonyl sulphide and nickel carbonyl vapour gradually increased in volume during five hours at the ordinary temperature from 46 c.c. to 52 c.c., but further increase was extremely slow.

In the two-bulb apparatus described above, 272 mm. of carbonyl sulphide, mixed with 102 mm. of nickel carbonyl, gave a final pressure of 260 mm., whereas complete reaction would have produced a pressure of 340 mm.

An alcoholic solution of carbonyl sulphide, mixed with nickel carbonyl, did not evolve gas or deposit solid at the ordinary temperature, but did so at 100°.

Hence it would appear that this reaction is of the same kind as that which takes place between nickel carbonyl and carbon disulphide, that is, it is incomplete, and this is explicable in the same way.

Allyl sulphide, thiophen, ethyl trithiocarbonate, ethyl dithiocarbonate, and thiocarbamide all react with nickel carbonyl to produce brown or black deposits. The reaction with thiophen and thiocarbamide is but slight; that which takes place with the other three compounds produced a brown deposit quite unlike the deposit of nickel sulphide obtained from carbon disulphide.

Nickel carbonyl reacts very readily with thiocarbonyl chloride in the cold, and this reaction led to the isolation of carbon monosulphide, which has already been described.

Iron carbonyl, liquid or vapour, does not react with carbon disulphide at the ordinary temperature, but does so slowly at 100°. This is another instance of the greater stability of the iron carbonyl.

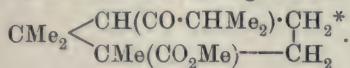
CIX.—*The Action of the Grignard Reagent on Camphoric and isoCamphoric Esters.*

By YŪJI SHIBATA.

IN a recent paper on the action of the Grignard reagent on *o*-phthalic esters (Trans., 1909, **95**, 1449) it was shown that the two CO_2R groups in these esters, unlike those in succinic and terephthalic esters, exert steric hindrance when the Grignard reaction is carried out, with the effect that derivatives of phthalide, or, as is more often the case, of phthalan are produced. In the case of succinic and terephthalic esters, the normal product of the reaction is a glycol, and it was pointed out that this difference in the action of the Grignard reagent on the esters of *o*-phthalic acid on the one hand, and on those of succinic and terephthalic acids on the other, was most probably due to the fact that the two CO_2R groups in *o*-phthalic esters are in the *cis*-position, whilst those in succinic and terephthalic esters are in the *trans*-position. It was further shown that, from the point of view thus attained by the study of the action of the Grignard reagent on *o*-phthalic esters, Graebe's space formula for benzene is to be preferred to all others.

In order to obtain, if possible, further confirmation of the view thus expressed, the behaviour of camphoric and *isocamphoric* esters toward the Grignard reagent has now been studied, these being known clearly as the *cis-trans*-isomerides. If the assumption is true that the two CO_2R groups in the *cis*-position exert steric hindrance, whilst those in the *trans*-position do not, then by the action of the Grignard reagent, camphoric esters should produce campholides, analogous to the phthalides, whilst *isocamphoric* esters should produce glycols or some other non-condensed hydroxyl derivatives.

This anticipation has, in fact, been fully confirmed, except in the case of the action of magnesium *isopropyl* iodide on dimethyl camphorate. In this case a substance has been obtained which is considered to be a ketonic ester having the constitution:



It is known that *isoalkyl* groups generally exert a more remarkable steric influence than the normal ones (compare Davis, Trans.,

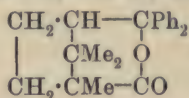
* The compounds of analogous constitution, *o*-acylbenzoic acids, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{COR}$, have been recently synthesised by the action of the Grignard reagent on phthalic acid by H. Simonis and K. Arand (*Ber.*, 1909, **42**, 3721; compare also A. Guyot and J. Catel, *Bull. Soc. chim.*, 1906, [iii], **35**, 551).

1909, **95**, 1397), and it is highly probable that here also the first isopropyl group which has entered into reaction with dimethyl camphorate has hindered the addition of a second molecule of the Grignard reagent, thus producing a ketonic ester, or, in other words, stopping the reaction at its first stage.

The Action of Magnesium Phenyl Bromide on Dimethyl d-Camphorate.

Dimethyl *d*-camphorate, prepared from *d*-camphoric acid and methyl sulphate according to Riedel's method (D.R.-P. 189840 of 1906; 196152 of 1908), boils at 147—150°/10 mm., or at 162—164°/29 mm., whilst Riedel gives its boiling point as 145—147°/20 mm. The sample was, therefore, analysed. (Found, C=62·87; H=8·78. Calc., C=63·10; H=8·85 per cent.)

The reaction between dimethyl camphorate and magnesium phenyl bromide was carried out in precisely the same manner as in the case of diethyl phthalate (Trans., 1909, **95**, 1452). An ethereal solution of the ester was added to magnesium phenyl bromide in the proportion of 1 to 4 molecules, and the product, obtained by decomposing the resulting solution with ice and dilute sulphuric acid, was distilled in a current of steam to remove the excess of bromobenzene and diphenyl. After crystallisation from alcohol, small, colourless, needle-shaped crystals, melting at 154—155°, were obtained. They are readily soluble in ether, benzene, carbon disulphide, acetone, chloroform, or hot alcohol, and sparingly so in cold alcohol or light petroleum. On analysis, the results obtained agreed with those required by *diphenylcampholide*,



0·1541 gave 0·4664 CO₂ and 0·1043 H₂O. C=82·54; H=7·75.

C₂₂H₂₄O₂ requires C=82·45; H=7·56 per cent.

That this substance is diphenylcampholide was proved by the action of alcoholic potash and of nitric acid on it.

Diphenylcampholide dissolved in alcohol was heated on a water-bath for about twenty hours with an excess of alcoholic potash. On adding a large amount of water, a small quantity of the original substance separated out. The filtrate was evaporated with repeated additions of water to remove the alcohol, and the aqueous solution was acidified with hydrochloric acid. The acid which was precipitated was converted into its barium salt, and this, after being dried at 120°, was analysed, and proved to be *barium diphenylhydroxycampholate*, (OH·CPh₂·C₈H₁₄·CO₂)₂Ba:

0.2458 gave 0.0699 BaSO₄. Ba = 16.73.

C₄₄H₅₀O₆Ba requires Ba = 16.92 per cent.

Diphenylhydroxycampholic acid, obtained by the hydrolysis of diphenylcampholide, being a γ -hydroxy-acid, easily yields a lactone. A small quantity of the acid was heated in an air-bath at 100° until constant weight was attained. The product was then analysed:

0.2339 gave 0.7009 CO₂ and 0.1587 H₂O. C = 81.73; H = 7.41.

C₂₂H₂₄O₂ requires C = 82.45; H = 7.56 per cent.

Thus, by merely heating to 100°, the lactone was formed. The same result was also obtained by heating the acid with an excess of acetic anhydride on a water-bath for about five hours.

Diphenylcampholide dissolves easily in fuming nitric acid with a considerable evolution of heat. The brown precipitate obtained on adding water to the solution, when crystallised from chloroform in the presence of animal charcoal, gave small, yellow crystals melting at 224—225°. These were soluble in chloroform, but insoluble in alcohol, ether, or light petroleum:

0.1275 gave 0.2997 CO₂ and 0.0531 H₂O. C = 64.11; H = 4.66.

0.1873 „ 11.12 N₂ at 18° and 760 mm. N = 6.82.

C₂₂H₂₂O₆N₂ requires C = 64.36; H = 5.41; N = 6.83 per cent.

The substance was therefore *dinitrodiphenylcampholide*.

Diphenylcampholide is very stable toward the action of oxidising agents. Thus, even when it was heated with chromic acid mixture to 150—155° for about twenty hours, only a very small portion of the substance was attacked, and, on repeated recrystallisation from alcohol, a small quantity of a substance melting at 200° was isolated, but the quantity of it was so small that further investigation was impossible.

The Action of Magnesium Ethyl Iodide on Dimethyl d-Camphorate.

As the product of this reaction, a yellow oil was obtained, the main part of which distilled (I) at 170—172° under 6—7 mm. pressure, or (II) at 176—178° under 16 mm. pressure:

(I) 0.2749 gave 0.7489 CO₂ and 0.2619 H₂O. C = 74.30; H = 10.65.

(II) 0.2362 „ 0.6437 CO₂ „ 0.2257 H₂O. C = 74.32; H = 10.68.

C₁₄H₂₄O₂ requires C = 74.93; H = 10.79 per cent.

$$\begin{array}{c} \text{CH}_2 \cdot \text{CH} - \text{CEt}_2 \\ | \quad | \quad | \\ | \quad \text{CMe}_2 \quad \text{O} \\ | \quad | \quad | \\ \text{CH}_2 \cdot \text{CMe} - \text{CO} \end{array}$$

Diethylcampholide, crystallises in small plates,

melting at 37—38°, and is soluble in alcohol, ether, light petroleum, chloroform, benzene, acetone, or carbon disulphide.

Long needles were obtained as the product of the action of

alcoholic potash on diethylcampholide, which melted at 90—98°. They were dissolved in alkali, and reprecipitated with hydrochloric acid, but no sharper melting point was observed. As the substance was scanty, no further study of it was attempted.

Diethylcampholide was heated with chromic acid mixture on a water-bath for five hours. The oxidation was accompanied by a brisk evolution of gas, and, on cooling, the oily substance solidified into fine needles. These were repeatedly recrystallised from dilute alcohol, when lustrous, feathery crystals, melting at 60°, were obtained. The substance is very readily soluble in alcohol, ether, benzene, chloroform, carbon disulphide, acetone, or light petroleum:

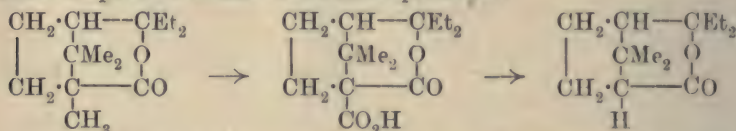
0.1039 gave 0.2834 CO₂ and 0.0994 H₂O. C=73.68; H=10.60.

0.2532, in 17.56 benzene, gave $\Delta t = -0.335^\circ$. M.W.=215.2.

C₁₃H₂₂O₂ requires C=74.21; H=10.56 per cent. M.W.=210.2.

The molecular weight of the substance was determined by the cryoscopic method.

On comparing this formula, C₁₃H₂₂O₂, with that of the original substance, C₁₄H₂₄O₂, it is seen that no increase in oxygen, but a loss of CH₂, was effected by the oxidation. This means that one of the three methyl groups in the camphor molecule had been replaced by a hydrogen atom, and the following scheme of the oxidation process seems to be most probable:



The compound is therefore probably *diethylapocampholide*. That this substance is a lactone may easily be proved by the action of alcoholic potash on it, whereby, after the usual treatment, a white precipitate was obtained on acidification. This crystallised overnight in feathery needles, melting at 60°:

0.0797 gave 0.2173 CO₂ and 0.0770 H₂O. C=74.36; H=10.80.

C₁₃H₂₂O₂ requires C=74.21; H=10.56 per cent.

The substance is, no doubt, nothing but the original substance, and the hydroxy-acid, first produced by the action of alcoholic potash, must have been converted into its lactone by the action of an excess of hydrochloric acid.

The Action of Magnesium Methyl Iodide on Dimethyl d-Camphorate.

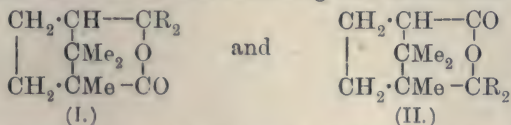
By the action of magnesium methyl iodide on dimethyl camphorate, carried out in the usual manner, an oily substance was obtained, almost all of which distilled in a current of steam. The

oil was extracted from the distillate by means of ether, and was fractionated under 10 mm. pressure. The main part distilled at 145—147.5° as a colourless oil with a faint odour like that of turpentine. On analysis, it gave the following results, agreeing well with the composition of dimethylcampholide:

0.3520 gave 0.9434 CO₂ and 0.3226 H₂O. C = 73.10; H = 10.25.

C₁₂H₂₀O₂ requires C = 73.39; H = 10.30 per cent.

G. Komppa (*Ber.*, 1908, **41**, 1039) obtained dimethylcampholide in a crystalline form, melting at 83.5—85°, by the action of magnesium methyl iodide on camphoric anhydride. In campholides, the existence of the following two isomerides is possible:



and, in fact, J. Houben (*Ber.*, 1908, **41**, 1580) obtained both of the two isomerides of dibenzylcampholide by the action of magnesium benzyl chloride on camphoric anhydride. In the case of dimethylcampholide, Komppa's crystalline form and the oily one described above will probably be found to correspond with these two forms. Komppa gave formula I to his dimethylcampholide without any remark on this point. I am, however, inclined to believe that my oily substance has formula I, and Komppa's crystalline one has formula II.

As will be described later, the action of magnesium phenyl bromide on dimethyl isocamphorate results in the formation of methyl diphenylhydroxyisocampholate, HO·CPh₂·C₈H₁₄·CO₂Me, one of the two ester groups remaining unattacked. In this case, from the point of view of steric influence, it is most natural to regard the unattacked ester group as one in union with that carbon atom which carries a methyl group with it. In the case of the formation of dialkyl (aryl) campholides, the same theory must also hold true, although the intermediate product, methyl dialkyl(aryl)-hydroxycampholate, could not be isolated, or, in other words, the campholides obtained by the action of the Grignard reagent on camphoric esters must have formula I. Again, it is also most probable that in the formation of two isomeric campholides from camphoric anhydride, that with formula I will be obtained in better yield than the other. In fact, Komppa states in his paper that he obtained an oily substance along with the crystalline dimethylcampholide, the former being in far larger quantity than the latter. He did not, however, further examine the oily substance, which should have contained the oily modification of the campholide.

An alcoholic solution of dimethylcampholide was treated with

an excess of alcoholic potash in the usual manner. The oil obtained on acidification was fractionated, when the main part of it passed over at 165—166°/16 mm. :

0.2055 gave 0.5451 CO₂ and 0.1887 H₂O. C=72.36; H=10.27.

C₁₂H₂₀O₂ requires C=73.39; H=10.30 per cent.

The oil thus separated by acidifying the alkaline solution is no more soluble in alkali. This fact and the results of the analysis show that the oil is the original dimethylcampholide, dimethylhydroxycampholic acid, formed by the hydrolysis of the campholide, having been converted into its lactone by the action of the hydrochloric acid.

The Action of Magnesium isoPropyl Iodide on Dimethyl d-Camphorate.

The product of this reaction is a colourless, viscous oil, with a feeble odour somewhat resembling that of camphor. On fractionation, it distilled at 140—142°/7 mm., or at 159—160°/20—21 mm.:

0.3177 gave 0.8220 CO₂ and 0.2716 H₂O. C=70.56; H=9.56.

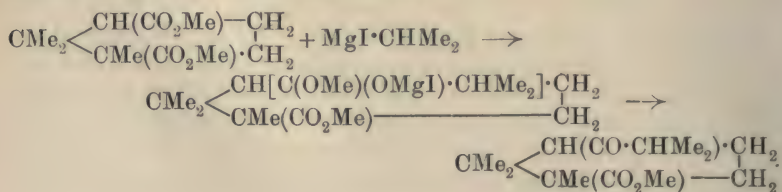
0.3126 „ 0.8069 CO₂ „ 0.2653 H₂O. C=70.35; H=9.48.

C₁₄H₂₄O₃ requires C=70.00; H=10.00 per cent.

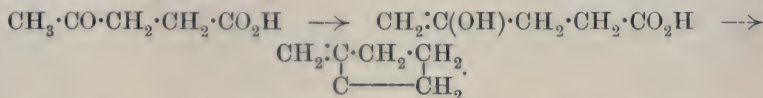
The oil was dissolved in benzene and shaken with an acid solution of potassium permanganate (5 per cent.). On removing the benzene, an oily substance was obtained, which was fractionated. The portion distilling at about 150°/7 mm. gave a considerable quantity of crystals on cooling, which were recrystallised from alcohol. The colourless needles thus obtained melted at 224—225°, and analysis showed that the substance was camphoric anhydride. (Found, C=65.98; H=7.82. Calc., C=65.90; H=7.74 per cent.)

The action of alcoholic potash on the substance C₁₄H₂₄O₃ also gave camphoric anhydride.

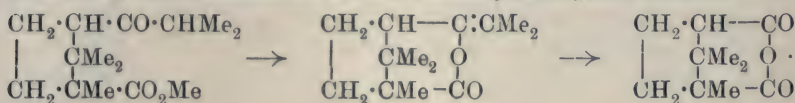
These changes can easily be explained if the constitution *methyl 1:2:2-trimethyl-3-isobutyrylcyclopentane-1-carboxylate* be assigned to the substance C₁₄H₂₄O₃, as stated in the introductory part, its formation from dimethyl camphorate and magnesium isopropyl iodide being represented as follows:



As is known, a γ -ketonic acid, like acetylpropionic acid, is easily converted into an unsaturated lactone by long heating, according to the following scheme:



In the formation of camphoric anhydride from the above substance $\text{C}_{14}\text{H}_{24}\text{O}_3$ by the action of potassium permanganate and of alcoholic potash, dimethylmethylenecampholide might first be formed, the above δ -ketonic ester having undergone a change similar to this change of γ -ketonic acids, whence camphoric anhydride is formed by the elimination of the dimethylmethylene residue:



*The Action of Magnesium Phenyl Bromide on Dimethyl
l-isoCamphorate.*

l-isoCamphoric acid was prepared from *d*-camphoric acid by Aschan's method (*Ber.*, 1889, **27**, 2005). The neutral methyl ester of this acid, hitherto unknown, was prepared by a method similar to that of J. D. Riedel (*loc. cit.*) for the preparation of camphoric esters. The *dimethyl* ester is a colourless, viscous oil, boiling at $165\text{--}170^\circ/37\text{--}38$ mm.:

0.2245 gave 0.5175 CO_2 and 0.1760 H_2O . $\text{C}=62.87$; $\text{H}=8.80$.

$\text{C}_{12}\text{H}_{20}\text{O}_4$ requires $\text{C}=63.10$; $\text{H}=8.85$ per cent.

The reaction between this ester and magnesium phenyl bromide was carried out in the same way as in the case of dimethyl camphorate, and a crystalline substance was obtained. On recrystallisation from alcohol, colourless needles, melting at $105\text{--}106^\circ$, separated, which consisted of *methyl diphenylhydroxyiso-campholate*:

0.1831 gave 0.5261 CO_2 and 0.1365 H_2O . $\text{C}=78.36$; $\text{H}=8.33$.

$\text{C}_{23}\text{H}_{28}\text{O}_3$ requires $\text{C}=78.36$; $\text{H}=8.01$ per cent.

The substance is readily soluble in benzene, ether, carbon disulphide, chloroform, or acetone, moderately so in alcohol or glacial acetic acid, and insoluble in light petroleum.

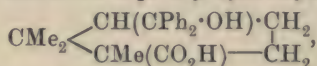
The alcoholic solution of the ester was boiled with an excess of alcoholic potash. On diluting the mixture with a large amount of water, a considerable quantity of the original ester separated out. The filtrate was evaporated to remove the alcohol, and the alkaline solution was acidified with hydrochloric acid. The white pre-

cipitate thus obtained was recrystallised from dilute alcohol, when lustrous, scaly crystals, melting at 214° , separated:

0.1323 gave 0.3797 CO_2 and 0.0944 H_2O . $\text{C}=78.27$; $\text{H}=7.98$.

$\text{C}_{22}\text{H}_{26}\text{O}_3$ requires $\text{C}=78.02$; $\text{H}=7.74$ per cent.

The substance is therefore *diphenylhydroxyisocampholic acid*,



a *trans*-acid, not forming its lactone easily, as is the case with *cis*-acids.

The preparation of dimethyl isocamphorate being laborious, further examination of the action of other Grignard reagents with this ester was not attempted.

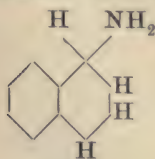
THE CHEMICAL INSTITUTE OF THE COLLEGE OF SCIENCE,
IMPERIAL UNIVERSITY OF TOKYO.

CX. — The Absorption Spectra of 1:4-Dihydronaphthalene and 1:2:3:4-Tetrahydronaphthalene.

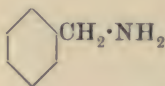
By A. G. G. LEONARD, B.Sc. (1851 Research Scholar).

ABOUT the year 1889 Bamberger prepared a large number of reduction products from naphthalene and its substituted derivatives. He showed that when reduction was confined to one of the nuclei in the naphthalene molecule the properties of the compounds so produced were in very close agreement with those of similarly constituted benzene derivatives.

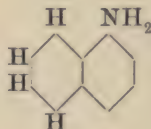
Thus, *ac*-tetrahydronaphthylamine (I) resembled benzylamine (II), whereas *ar*-tetrahydronaphthylamine (III) corresponded in properties with xylidine (IV).



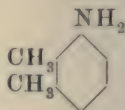
(I.)



(II.)



(III.)



(IV.)

It was thought that a study of some of the absorption spectra of such reduced compounds might be of interest in connexion with the above results.

The spectra of the 1:4-di- and the 1:2:3:4-tetrahydro-derivatives were examined in order to determine whether such a marked difference from the absorption spectrum of naphthalene

existed as would account for the well-known change in chemical properties produced by the introduction of hydrogen atoms into the naphthalene molecule. Furthermore, if such a difference were found, it would be of interest to observe to what extent the curves of the hydrides were comparable with the closely related di-substituted benzene, *o*-xylene.

EXPERIMENTAL.

1:4-Dihydronaphthalene.—This was prepared according to Bamberger and Lodter's method (*Ber.*, 1887, **20**, 1705), which is the only way of obtaining the substance quite free from naphthalene. The sample used for determining the spectrum was redistilled twice over sodium, and boiled constantly at 212°/760 mm.

1:2:3:4-Tetrahydronaphthalene.—For the preparation of this substance, Bamberger and Kirschelt's method (*Ber.*, 1890, **23**, 1561) was employed. It boiled constantly at 210°/768 mm.

To avoid oxidation of the hydrides during the preparation of the solutions for the spectra, they were weighed out in small, sealed bulbs. The bulbs were then broken under alcohol, and the solutions diluted to the requisite volume.

Description of the Spectra.

1:4-Dihydronaphthalene exhibits a broad absorption band between $1/\lambda$ 3470 and $1/\lambda$ 4314. It occurs at the same concentrations as those at which the bands of naphthalene appear, but the absorption is shifted about 100 Ångström units towards the more refrangible end of the spectrum, that is, nearer to the region of the benzene absorption bands.

1:2:3:4-Tetrahydronaphthalene also shows a broad band lying between $1/\lambda$ 3530 and $1/\lambda$ 4290; it corresponds closely with the band of the dihydride, but in its general character displays an increased amount of general absorption.

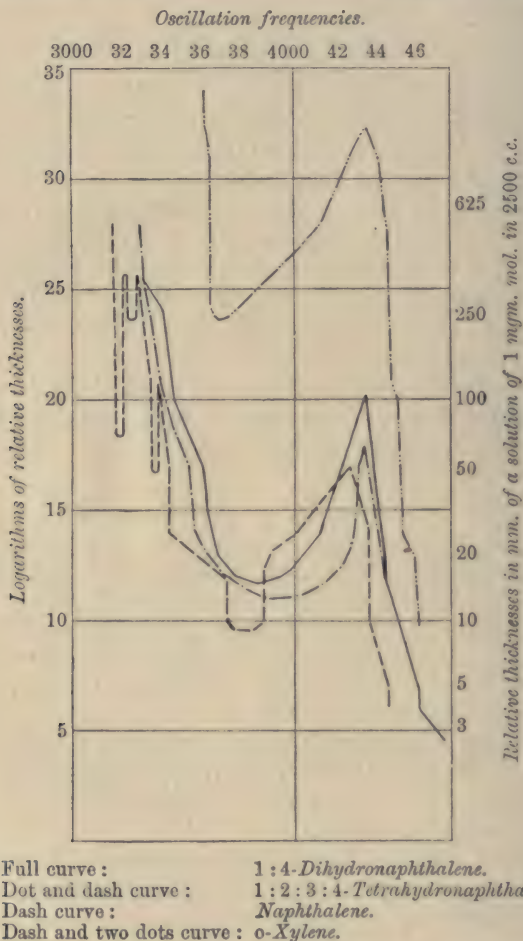
Naphthalene and *o*-xylene were examined by Hartley in 1885 (*Trans.*, **47**, 685), and the curves as then determined are here reproduced according to Baly's logarithmic method.

Discussion of the Results.

Since the curves of the two hydrides resemble one another so closely, they may, for purposes of comparison, be here considered together.

Hartley has shown (*Kayser's Handbuch der Spectroscopie*, Vol. III., p. 310) that, in general, increase of molecular weight

produces a shifting of absorption towards the less refrangible rays. Now, in the case of addition of hydrogen atoms to the naphthalene molecule, we find a shifting of the absorption towards the region of the benzene bands, that is, towards the more refrangible rays. This is obviously to be accounted for by a change from the more



complicated vibratory system of the naphthalene molecule to that of a molecule which may be regarded as that of an ortho-disubstituted benzene.

The fact that the band in the spectra of the hydrides appears at the same concentrations as the naphthalene band agrees with Hartley's observations on the absorption spectra of quinoline and tetrahydroquinoline (Trans., 1885, **47**, 685), the bands in the spectra

of the latter two appearing at similar concentrations. Now, it is known that aliphatic compounds possessing a ring structure exert, in general, a much more powerful general absorption than open-chain compounds of like molecular weight. In the case of the tetrahydride, we have an aliphatic ring produced by the union of a chain of four methylene groups to two ortho-carbon atoms of the benzenoid nucleus. This ring thus causes greatly increased general absorption, and so leads to the appearance of the benzenoid band at much smaller concentrations than those at which the band of *o*-xylene appears.

Conclusions.

1. The curves of 1:4-dihydronaphthalene and 1:2:3:4-dihydronaphthalene are shown to be similar to one another, and to occupy an intermediate position between the curves of naphthalene and *o*-xylene.

2. The spectra are those of a benzenoid nucleus as modified by the presence of an aliphatic ring.

3. Such spectra are in close agreement with the observed chemical properties of the two hydrides.

It is hoped at a later date to extend the work to an examination of the substances in a state of vapour.

In conclusion, I wish to express my thanks to Professor Hartley for his friendly interest during the course of the work.

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ROYAL COLLEGE OF SCIENCE,
DUBLIN.

CXI.—*The Existence of Racemic Compounds in Solution.*

By ALBERT ERNEST DUNSTAN and FERDINAND BERNARD THOLE.

IN a previous paper (Dunstan and Thole, *Trans.*, 1908, **93**, 1815) experimental evidence was brought forward which showed that, to a limited extent, racemic compounds were capable of existence in the dissolved condition. Bearing in mind the previous work of Clerk Ranken and Taylor (*Proc. Roy. Soc. Edin.*, 1907, **27**, 172), Perkin (*Trans.*, 1887, **51**, 362), and Marchlewski (*Ber.*, 1892, **25**, 1556), the existence of racemic tartaric acid in aqueous solution may be taken as amply substantiated, although under the most favourable conditions of concentration the amount present as such

is undoubtedly small. Considering the great importance of the subject, both from its bearing on stereochemistry and also on the general theory of solutions, the problem of the continued existence of racemic compounds has again been attacked, and the results are brought forward in the present paper. The following references are supplementary to those contained in the former communication.

Marchlewski (*Ber.*, 1895, **28**, 1611) pointed out that racemic acid at a concentration of 10—14 per cent. in aqueous solution has a lower specific volume than the corresponding active acids.

Küster (*Ber.*, 1898, **31**, 1847) determined the solubility of silver *l*-valerate, and found that this salt was less soluble than the inactive valerate; similar results were obtained with barium camphoronate. Kipping and Pope (*Proc.*, 1898, 219; *Trans.*, 1899, **36**, 1119) and Ladenburg (*Trans.*, 1899, **75**, 465) objected to such solubility determinations as being indecisive; whilst Roozeboom (*Zeitsch. physikal. Chem.*, 1899, **28**, 494) demonstrated the possibility of diagnosing racemism by investigating the respective solubilities of the supposed racemic compound alone and with excess of the active form (*d* or *l*).

The possibility of the free existence of a racemate at the temperature of its melting point has been worked out fully from the point of view of the Phase Rule (see Findlay's *Phase Rule*, 1908, p. 216).

Findlay and Hickmans (*Trans.*, 1907, **91**, 905) also have detected the existence of *l*-menthyl *r*-mandelate in the fused state, and in the same paper give a summary of previous work in this connexion. The same authors (*Trans.*, 1909, **96**, 1386) determined the solubility relationships of *l*-menthyl esters of the mandelic acids, and obtained an excellent confirmation of their earlier results, proving that *l*-menthyl *r*-mandelic acid is stable in the saturated solution down to -15° .

Kipping (*Trans.*, 1909, **95**, 408, and 1386 footnote) considered that racemic compounds had a free existence in the liquid state, seeing that *d*-hydrindamine *r*-mandelate was resolvable by crystallisation from aqueous solution, whilst *dl*-hydrindamine *d*-mandelate could not be so resolved.

The methods of Roozeboom above described are applicable to cases where fusion curves can be constructed or where saturated solutions can be prepared, hence one or other is available in most instances. It is desirable, however, independently to obtain confirmation of these results, and also to investigate the possibility of the existence of racemic compounds in more dilute solutions. To this end the application of viscosimetry has been found eminently suitable, since the internal friction of a liquid is very essentially a molecular function.

The apparatus used has been described in previous papers, and all the conditions laid down hitherto have been observed (Trans., 1909, **95**, 1558; 1907, **91**, 1730; 1905, **87**, 11; 1904, **85**, 817). When working with volatile or hygroscopic solvents, it is of considerable importance to prevent loss or contamination. This can be avoided by attaching guard tubes to the limbs of the viscosimeter. These tubes contain glass wool loosely packed and soaked with the liquid or solution under examination (see Findlay, *Zeitsch. physikal. Chem.*, 1909, **69**, 203). The temperature of experiment was throughout 25° , and was kept constant to 0.02° .

The sec.-Octyl Hydrogen Phthalates.

Kahlbaum's *sec.*-octyl alcohol was resolved by being converted into its hydrogen phthalic ester, and this into the *l*-brucine salts (Pickard and Kenyon, Trans., 1907, **91**, 2058). The *dl*-ester melted at 55 – 56° , the *l*-brucine *d*-octyl phthalate melted at 151° , and the *d*-octyl hydrogen phthalate melted at 74 – 75° . We are indebted to Mr. T. P. Hilditch, who kindly determined the rotations of two specimens of the *d*-octyl hydrogen phthalate.

I. 1 per cent. in chloroform solution, in a 1-dcm. tube, at 22° , gave $\alpha_D + 0.428^{\circ}$, whence $[\alpha]_D + 42.80^{\circ}$.

II. 1 per cent. in chloroform solution, in a 1-dcm. tube, at 22° , gave $\alpha_D + 0.406^{\circ}$, whence $[\alpha]_D + 40.60^{\circ}$.

Pickard (*loc. cit.*) gives $[\alpha]_D + 42.94^{\circ}$.

d-Octyl alcohol therefrom: $[\alpha]_D = 9.27^{\circ}$.

The *l*-ester was not purified so thoroughly, and was only used as a check. It melted at 71° , and had $[\alpha]_D - 21.6^{\circ}$, hence it contained about 75 per cent. of the active ester.

In these experiments a weighed amount of the ester was dissolved in a weighed quantity of pure benzene (b. p. 80.5° over sodium). The esters were recovered from the solutions, and were found to be

TABLE I.

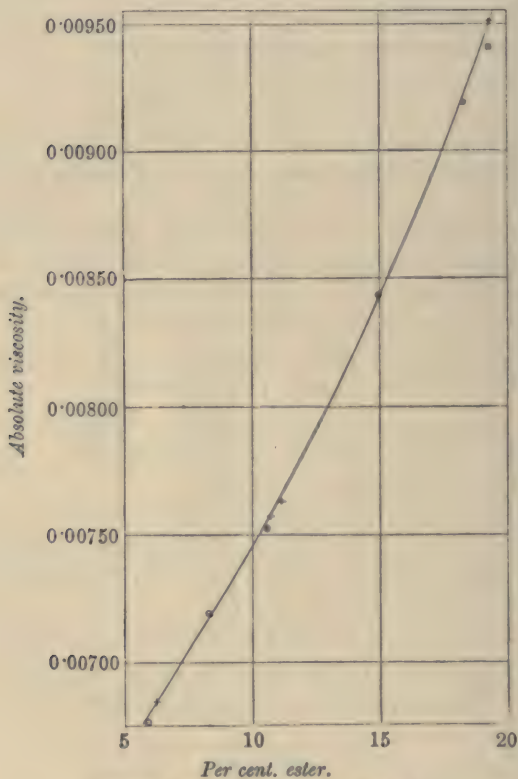
The Octyl Hydrogen Phthalates in Benzene.

Per cent. ester.	Time of flow in seconds.	Density 25/4.	Absolute viscosity.
<i>r</i> 5.86	207.9	0.8826	0.006767
<i>r</i> 8.24	220.0	0.8863	0.007189
<i>r</i> 10.61	229.2	0.8901	0.007520
<i>r</i> 14.95	255.1	0.8966	0.008432
<i>r</i> 15.28	260.0	0.8977	0.008604
<i>r</i> 18.29	276.5	0.9017	0.009190
<i>d</i> 6.18	210.1	0.8836	0.006844
<i>d</i> 10.71	231.2	0.8887	0.007575
<i>d</i> 11.16	233.5	0.8866	0.007631
<i>d</i> 19.44	285.4	0.9054	0.009525
<i>l</i> 19.29	282.4	0.9046	0.009418

unaltered. From melting-point experiments it seems that a racemic compound is not formed, although the quantity of the esters at our disposal was not sufficient to carry out a satisfactory series of determinations.

The foregoing results can be represented satisfactorily by one regular curve (Fig. 1); it follows, then, that under the conditions

FIG. 1.



© = Racemic.

+ = Dextro.

□ = Laevo.

of these experiments, racemic octyl hydrogen phthalate exists merely as a mixture of the active forms, and up to a concentration of 19 per cent. in a non-dissociating solvent there is no sign of any difference in viscosity between the active and inactive forms.

The Mandelic Acids.

The *r*-mandelic acid was obtained from Schuchardt and Kahlbaum. The specimens we received were free from nitrogen,

and, after several crystallisations from dry benzene, melted at 118.5° . The *l*-mandelic acid was partly made from amygdalin and partly purchased from Schuchardt. It was purified by several crystallisations from benzene, and melted at 133° . We are indebted to Mr. T. P. Hilditch for the measurement of rotation. He found for a 2 per cent. solution in alcohol, $\alpha_D -6.918^{\circ}$, whence $[\alpha]_D -154.95^{\circ}$.

The *d*-mandelic acid was kindly furnished by Mr. Tutin, to whom our thanks are due. It was prepared from the cinchonine salt, and melted at 133° . Mr. Tutin found that 0.4020 gram, made up in 20 c.c. of water in a 2-dcm. tube, had $\alpha_D +6.15'$, whence $[\alpha]_D +155.5^{\circ}$. Kipping (*Trans.*, 1909, **94**, 416) gives $[\alpha]_D +156.0^{\circ}$.

Adriani (*Zeitsch. physikal. Chem.*, 1900, **33**, 453) has already shown that inactive mandelic acid exists as a racemic compound at its melting point, but the fusion curve he obtained is strikingly illustrative of the slight degree of association between the active forms. Similarly, the partly racemic *l*-menthyl *r*-mandelate examined by Findlay and Hickmans only exists to the extent of 35 to 50 per cent. at its melting point. This being so, it is not surprising that no difference in viscosity was found with dilute aqueous solutions, since an almost complete dissociation must have taken place.

TABLE II.

The Mandelic Acids in Water.

Per cent. acid.	Time of flow in seconds.	Density 25/4.	Absolute viscosity.
<i>l</i> 5.10	276.9	1.009	0.01030
<i>l</i> 7.27	289.1	1.014	0.01081
<i>l</i> 9.49	307.1	1.019	0.01153
<i>l</i> 10.30	315.5	1.022	0.01188
<i>r</i> 4.02	265.5	1.006	0.00984
<i>r</i> 5.38	275.9	1.009	0.01026
<i>r</i> 7.78	294.3	1.013	0.01099
<i>r</i> 8.17	295.8	1.016	0.01108
<i>r</i> 11.22	321.8	1.024	0.01215
<i>d</i> 7.78	294.5	1.013	0.01100

In the expectation that a solvent having a less dissociating power than water would be of use in repressing the dissociation, experiments have been made with solutions of the mandelic acids in pyridine, although it is true that this liquid possesses disruptive powers, probably in the case in point by exercising its saligenic properties. A reference to table III and Fig. 2 will show that the desired end was not attained, since the experimental results all lie sufficiently near one regular curve.

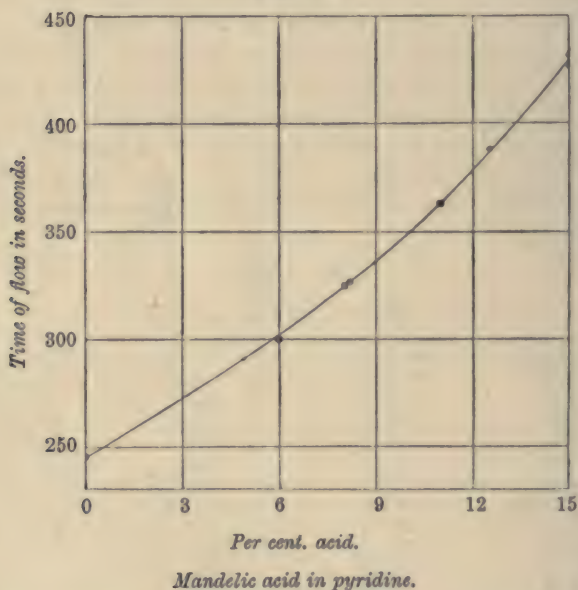
TABLE III.

The Mandelic Acids in Pyridine.

The pyridine used was obtained by the rectification of a large amount of the crude coal-tar product. Using a long rod and disk column a fraction was obtained boiling steadily at 116° :

Per cent. acid.	Time of flow in seconds.	Per cent. acid.	Time of flow in seconds.
0.00	244.4	<i>r</i> 6.04	300.0
<i>l</i> 8.05	325.2	<i>r</i> 8.19	326.0
<i>l</i> 11.02	363.0	<i>r</i> 12.53	388.6
<i>l</i> 15.04	426.9	<i>r</i> 15.03	431.6

FIG. 2.



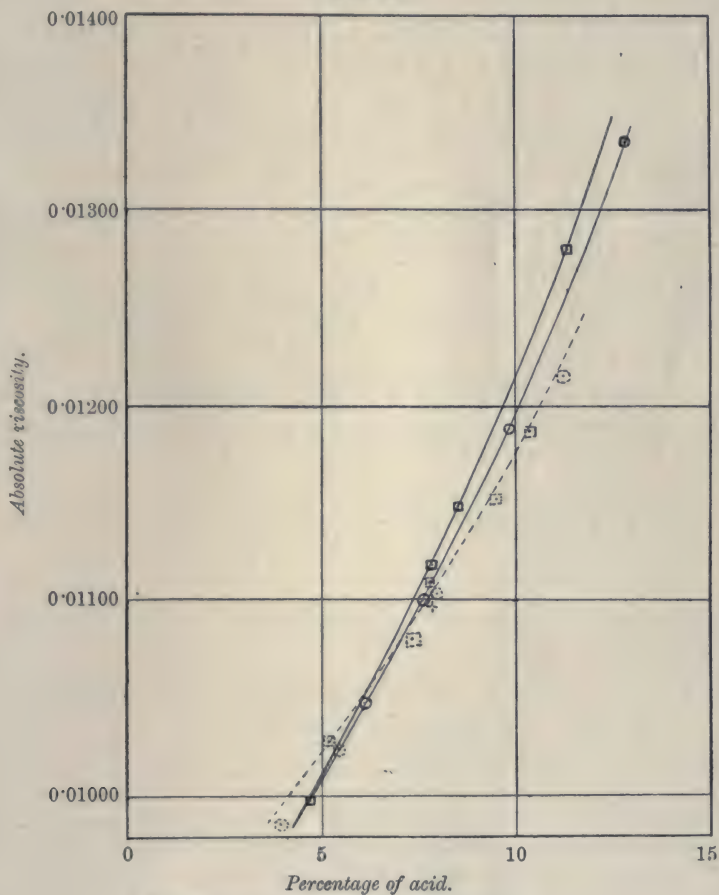
When, however, the mandelic acids were dissolved in amyl acetate (b. p. 137.5° , fractionated from the "pure" ester), results were obtained which lead to the view that the racemic compound is present in solution, although still to a very small extent.

TABLE IV.

The Mandelic Acids in Amyl Acetate.

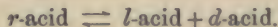
Per cent. acid.	Time of flow in seconds.	Density 25/4.	Absolute viscosity.
<i>r</i> 6.12	324.5	0.8764	0.01048
<i>r</i> 7.64	338.6	0.8813	0.01100
<i>r</i> 9.86	363.0	0.8880	0.01188
<i>r</i> 12.88	403.3	0.8976	0.01335
<i>l</i> 4.72	310.6	0.8722	0.009985
<i>l</i> 7.93	343.6	0.8823	0.01118
<i>l</i> 8.55	353.2	0.8843	0.01149
<i>l</i> 11.39	388.7	0.8933	0.01280

FIG. 3.

Dotted curve: *Mandelic acids in water.*Full " : " " *amyl acetate.*□ = *Laevo.*○ = *Racemic.*+ = *Dextro.*

Although it would be possible to represent the above figures on one regular curve, it is obvious that the values for the racemic mandelic acid all lie a little below those of the *l*-compound (Fig. 3). It should be borne in mind, also, that the divergence of the two curves increases with concentration precisely as was shown for the similar case of the tartaric acids (*loc. cit.*).

A further endeavour to substantiate the previously published work on the tartaric acids was made on the basis of the law of mass action. If racemic acid dissociates into its active components, there should exist the equilibrium represented in the equation :



If, then, a solution of the *r*-acid is made up in the presence of either antipode, the dissociation should be depressed. In accordance with this it was found that a solution of *d*-tartaric acid containing 13.04 per cent. of the acid had the viscosity 0.01248, whereas a solution containing 8.69 per cent. racemic acid and 4.35 per cent. *d*-tartaric acid had the viscosity 0.01240, that of a solution of racemic acid of the same concentration being 0.01237.

It is worthy of notice that Bruni and Padoa (*Atti R. Accad. Lincei*, 1902, [v], 11, i, 212) found at low concentrations that active and *r*-esters of diacetyltartaric acids gave normal molecular weights in benzene, xylene, and ethylene dibromide solutions, but, with increasing concentration, association took place. In the presence of excess of an active form, they concluded that the racemic compound existed. Bruni and Finzi (*Atti R. Accad. Lincei*, 1904, [v], 13, ii, 349) further demonstrated the presence of a cryohydrate containing the racemic compound by the effect on it of the active forms.

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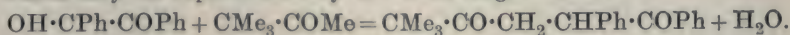
CXII.—*The Action of Methyl tert.-Butyl Ketone on Ketols. Part I.*

By ALFRED ARCHIBALD BOON.

THE action of methyl *tert.*-butyl ketone on ketols (simple and mixed) has not been studied. With this object in view, the author thought it might be of interest to investigate the action of pinacolone on furoin, especially as the constitution usually assigned to the former compound was not long ago called into question by Delacre (*Compt. rend.*, 1896, 122, 1202; 1896, 123, 245; 1901, 133, 738).

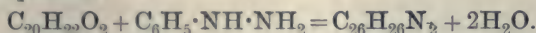
Furoin was chosen, as the author has been for some time studying the action of ketones on furan compounds.

In spite of many experiments, under varying conditions, methyl *tert.*-butyl ketone could not be condensed with furoin. In all these experiments potassium cyanide was used as the condensation agent. On benzoin, however, pinacolone was found to act in the presence of potassium cyanide, the resulting compound being the γ -diketone, *desylpinacolone* (α -*tert.*-butyryl- β -benzoylphenylethane), a reaction which may be represented by the following scheme:

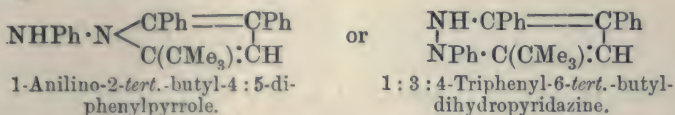


This compound melts at 110—111°, and gives the pyrrole-red reaction. By means of the action of hydroxylamine hydrochloride on it, two oximes were isolated, namely, a *mono-oxime*, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}$, and a *dioxime*, $\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2$. Both these compounds are colourless, and were obtained in fair yields. The dioxime suffered decomposition at the temperature at which it melted (210°).

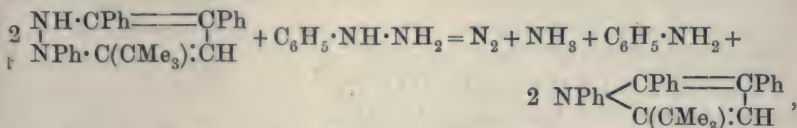
Only one compound was obtained sufficiently pure for examination when phenylhydrazine was allowed to act on desylpinacolone. Two other compounds were formed at the same time, but attempts to isolate these in a pure state did not meet with any degree of success. They appeared, however, to melt at about the same temperature as the compound which was obtained pure, namely, at 167—168°. The production of this substance takes place according to the following equation:



The compound $\text{C}_{26}\text{H}_{26}\text{N}_2$ may be represented by either of the following constitutional formulae:



As excess of phenylhydrazine was used in the preparation of the compound $\text{C}_{26}\text{H}_{26}\text{N}_2$, there was also the possibility of the following reaction taking place:



but in none of the author's experiments did this occur.

This pyrrole compound, $\text{C}_{26}\text{H}_{25}\text{N}$, was, however, obtained by the action of aniline on desylpinacolone. Although, as a rule, γ -diketones are easily converted into thiophen compounds, yet this does not appear to be the case with desylpinacolone.

Furan and pyrrole derivatives can be obtained from the γ -diketone, and these are described below.

EXPERIMENTAL.

Desylpinacoline (α -tert.-Butyryl- β -benzoylphenylethane),
 $\text{CMe}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHPh} \cdot \text{COPh}$.

Fifty grams of benzoïn are mixed with 25 grams of pinacoline, 200 grams of alcohol, 200 grams of water, and 10 grams of potassium cyanide, and boiled on a water-bath under reflux. As soon as an emulsion begins to form, the heating is stopped, and when the mixture is conveniently cool, 200 grams of absolute alcohol are added, and the boiling is continued. About twenty hours are required for the experiment.

The yellow, crystalline mass thus obtained is collected, washed with water, and boiled with methyl alcohol and animal charcoal. To the filtrate, which should be almost colourless, an equal volume of water is added, and the crystalline mass thus obtained is purified by crystallisation from dilute methyl alcohol:

0.1635 gave 0.4896 CO_2 and 0.1111 H_2O . $\text{C} = 81.67$; $\text{H} = 7.55$.

0.2128 „ 0.6357 CO_2 „ 0.1453 H_2O . $\text{C} = 81.47$; $\text{H} = 7.59$.

0.3730, in 43.88 of nitrobenzene, gave $\Delta t = -0.207^\circ$. $\text{M.W.} = 291$.

$\text{C}_{20}\text{H}_{22}\text{O}_2$ requires $\text{C} = 81.63$; $\text{H} = 7.48$ per cent. $\text{M.W.} = 294$.

Desylpinacoline melts at 110 — 111° . When crystallised from ethyl alcohol, it is obtained in very small needles. It is soluble in most organic solvents, and the average yield from the above materials is between 20 and 30 grams.

Action of Hydroxylamine on Desylpinacoline.

The *mono-oxime*, $\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}$.—Four parts of desylpinacoline are dissolved in boiling alcohol, and to the hot solution a mixture of 1 part of hydroxylamine hydrochloride and 1 part of sodium hydroxide, each dissolved in 10 parts of water, is added. The solution is now frequently shaken during the first hour after the addition of the above mixture, and is then kept for two days at the ordinary temperature. The crystals which are formed are washed with cold water and recrystallised from boiling alcohol.

The compound melts at 110 — 111° . It is very soluble in chloroform or ether, and dissolves in hot light petroleum or acetic acid. It is insoluble in alkalis:

0.1537 gave 0.4372 CO_2 and 0.1066 H_2O . $\text{C} = 77.58$; $\text{H} = 7.70$.

0.1811 „ 0.5153 CO_2 „ 0.1239 H_2O . $\text{C} = 77.60$; $\text{H} = 7.60$.

0.2089 „ 8.0 c.c. N_2 (moist) at 18° and 763 mm. $\text{N} = 4.54$.

$\text{C}_{20}\text{H}_{23}\text{O}_2\text{N}$ requires $\text{C} = 77.67$; $\text{H} = 7.44$; $\text{N} = 4.54$ per cent.

The *Dioxime*, $C_{20}H_{24}O_2N_2$.—Three parts of desylpinacolone are dissolved in about 75 c.c. of absolute alcohol. To the warm solution a mixture of 3 parts of sodium hydroxide, dissolved in 12 parts of water, and 3 parts of hydroxylamine hydrochloride, dissolved in 15 parts of water, is added. The pale yellow solution is well shaken, and then kept at the ordinary temperature for about a week. The crystalline deposit is frequently crystallised from boiling alcohol:

0.1965 gave 0.5337 CO_2 and 0.1286 H_2O . $C=74.07$; $H=7.27$.

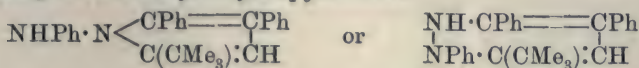
0.1500 „ 0.4058 CO_2 „ 0.1024 H_2O . $C=73.78$; $H=7.59$.

0.2178 „ 16.4 c.c. N_2 (moist) at 17° and 743 mm. $N=8.53$.

$C_{20}H_{24}O_2N_2$ requires $C=74.07$; $H=7.41$; $N=8.64$ per cent.

The dioxime melts at 210° , giving off bubbles of nitrogen. It dissolves in hot methyl alcohol, but is insoluble in ether, chloroform, or acetic acid.

Action of Phenylhydrazine on Desylpinacolone: Formation of 1-Anilino-2-tert.-butyl-4:5-diphenylpyrrole or 1:3:4-Triphenyl-6-tert.-butyldihydropyridazine.



Six parts of desylpinacolone are dissolved in 60 parts of warm glacial acetic acid. To the cold solution 7.5 parts of phenylhydrazine are added, and the mixture is heated on a water-bath for about five hours and then allowed to cool. The resulting compound is frequently crystallised from alcohol. The yield is very poor:

0.1530 gave 0.4786 CO_2 and 0.0931 H_2O . $C=85.31$; $H=6.76$.

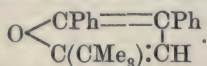
0.1771 „ 0.5351 CO_2 „ 0.1058 H_2O . $C=85.29$; $H=6.87$.

0.1835 „ 12.6 c.c. N_2 (moist) at 16° and 753 mm. $N=7.93$.

$C_{26}H_{26}N_2$ requires $C=85.25$; $H=7.10$; $N=7.65$ per cent.

The compound melts at $167-168^\circ$. It is soluble in light petroleum, chloroform, or ether, but insoluble in sodium hydroxide or hydrochloric acid.

Conversion of Desylpinacolone into 2-tert.-Butyl-4:5-diphenylfuran,



Desylpinacolone is dissolved with constant stirring in concentrated sulphuric acid. The mixture becomes slightly warm, and changes colour (brownish-red by reflected and yellowish-green by transmitted light). After two hours at the ordinary temperature, it is poured

into about twenty times its own volume of water, the mixture being stirred during this part of the operation. Globules of oil soon collect on the surface of the solution, which, on being kept for some time, furnish white, crystalline flakes. These are dried on a porous plate, and crystallised from boiling alcohol:

0.1568 gave 0.4984 CO_2 and 0.1034 H_2O . $\text{C}=86.69$; $\text{H}=7.33$.

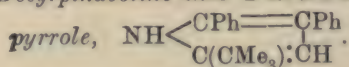
0.1766 „ 0.5618 CO_2 „ 0.1160 H_2O . $\text{C}=86.76$; $\text{H}=7.29$.

0.539, in 22.3 c.c. alcohol, gave $\text{E}=0.140^\circ$. $\text{M.W.}=269$.

$\text{C}_{20}\text{H}_{20}\text{O}$ requires $\text{C}=86.96$; $\text{H}=7.25$ per cent. $\text{M.W.}=276$.

The compound melts at $68-69^\circ$. It is soluble in chloroform, ether, glacial acetic acid, or light petroleum. When strongly heated it decomposes (the vapours, when viewed in thin layers, show a play of colours) (Trans., 1904, **85**, 1497).

Conversion of Desylpinacoline into 2-tert.-Butyl-4:5-diphenyl-



One part of desylpinacoline is added to 25 parts of alcohol which have been saturated with ammonia. The mixture is heated in a sealed tube between 160° and 200° until the solution turns a pink colour. When stirred with a large quantity of water, a brownish-red, gelatinous mass is produced, from which, on keeping, reddish-brown nodules are obtained. These are boiled with alcohol and animal charcoal, and the crystals thus obtained are recrystallised from alcohol:

0.1603 gave 0.5112 CO_2 and 0.1127 H_2O . $\text{C}=86.97$; $\text{H}=7.81$.

0.2204 „ 0.7040 CO_2 „ 0.1523 H_2O . $\text{C}=87.11$; $\text{H}=7.67$.

0.3288 „ 15 c.c. N_2 (moist) at 16° and 746 mm. $\text{N}=5.21$.

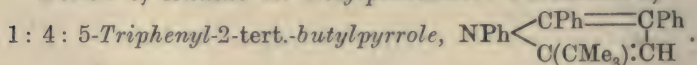
0.539, in 25.0 c.c. alcohol, gave $\text{E}=0.120^\circ$. $\text{M.W.}=280$.

$\text{C}_{20}\text{H}_{21}\text{N}$ requires $\text{C}=87.27$; $\text{H}=7.64$; $\text{N}=5.09$ per cent.

$\text{M.W.}=275$.

The compound melts at $98-99^\circ$. It is soluble in most organic solvents, and also in sodium hydroxide or hydrochloric acid.

Action of Aniline on Desylpinacoline: Formation of



Three parts of desylpinacoline are dissolved in 20 parts of glacial acetic acid. To this is added 1 part of freshly distilled aniline, and the mixture heated gently on the sand-bath for about eight hours. The crystals thus obtained are collected, dried on a porous plate, and recrystallised from alcohol:

0.1602 gave 0.5205 CO_2 and 0.1068 H_2O . $\text{C}=88.61$; $\text{H}=7.40$.

0.1800 „ 0.5854 CO_2 „ 0.1202 H_2O . $\text{C}=88.69$; $\text{H}=7.41$.

0.2047 „ 7.4 c.c. N_2 (moist) at 13° and 741 mm. $\text{N}=4.16$.

$\text{C}_{20}\text{H}_{25}\text{N}$ requires $\text{C}=88.89$; $\text{H}=7.12$; $\text{N}=3.99$ per cent.

The compound melts at $202-203^\circ$. It is sparingly soluble in ether, but dissolves in hot methyl alcohol, benzene, light petroleum, or chloroform.

Both the above pyrrole derivatives give the pyrrole-red reaction. As mentioned above, several attempts were made to obtain the thiophen compound $\text{C}_{20}\text{H}_{20}\text{S}$, but without success. Two of these experiments are indicated here.

When heated with half its weight of phosphorus pentasulphide in a sealed tube to about 200° , desylpinacoline yields a red, viscous mass, which, however, could not be crystallised. Nevertheless, after being well washed with water and dried on a porous plate, it had a strong, thiophen-like odour. It gave the indophenine reaction, at first giving a very dark green solution, which changed to a bluish-green colour on keeping. It is very probable that this viscous mass is an impure specimen of the thiophen compound.

Desylpinacoline, when heated with phosphorus pentasulphide at about 150° , either in open or sealed tubes, invariably gave a small quantity of the above furan derivative, $\text{C}_{20}\text{H}_{20}\text{O}$. Every care was taken in these experiments to have the materials dry and pure.

As the action of phenylhydrazine and of phosphorus pentasulphide on desylpinacoline promises to be of more than ordinary interest, the author intends studying these actions further, and extending his work to other ketols on lines similar to the present communication.

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CXIII.—*Behaviour of Two Salts with a Common Ion, when Dissolved in an Organic Solvent.*

By JAMES CHARLES PHILIP and HAROLD REUBEN COURTMAN.

So far as aqueous solutions are concerned, it is generally found that the solubility of an electrolyte is diminished by adding another electrolyte with a common ion, and increased by adding one which has no common ion. In the quantitative interpretation of this phenomenon, as well as of other properties of an aqueous solution of two salts, the electrolytic dissociation theory has been of signal service. Much

evidence has been accumulated in recent years by Walden and others showing that ionisation of salts occurs in organic solvents, and that the degree of ionisation, as in water, increases with dilution. It therefore becomes an interesting question whether the mutual relationship of two salts, when dissolved in an organic solvent, is similar to the relationship which they exhibit in aqueous solution, and whether the electrolytic dissociation theory is as serviceable in the one case as in the other.

One of the first points that come up for consideration in this connexion is the conductivity of the solution of the two salts and its relation to the conductivities of the separate salts. So far as aqueous solutions are concerned, this problem has been attacked theoretically and experimentally by a number of workers (Arrhenius, *Zeitsch. physikal. Chem.*, 1888, 2, 284; 1890, 5, 1; MacGregor, *Phil. Mag.*, 1896, 41, 276; Kay, *Proc. Roy. Soc. Edin.*, 1897, 22, 502; Barmwater, *Zeitsch. physikal. Chem.*, 1899, 28, 424; 1903, 45, 557; 1906, 56, 225; Sabat, *ibid.*, 1902, 41, 224). Various methods have been suggested by these investigators for calculating the conductivity of a solution of two electrolytes with a common ion from the conductivities of the separate electrolytes, but underlying all the methods is the assumption that the dissociation of each electrolyte in the mixed solution is approximately that which it would exhibit if it were present alone in the solution at a concentration equal to the sum of the concentrations of the two electrolytes.

In the present paper, the conductivity of a mixture of two salts with a common ion has been calculated from the conductivities of the separate salts in the way suggested by Barmwater. His method is based on the empirical rule formulated by Kohlrausch, according to which the equivalent conductivity of a binary salt in dilute aqueous solution is a linear function of the cube root of the concentration. This rule is expressed algebraically by the equation: $\lambda = \lambda_{\infty} - a\sqrt[3]{\eta}$, where a is a constant. If this equation is divided throughout by λ_{∞} , and $\frac{\lambda}{\lambda_{\infty}}$ is replaced by x , the degree of dissociation, we have:

$x = 1 - \frac{a}{\lambda_{\infty}} \sqrt[3]{\eta}$. For a given salt at a given temperature, $\frac{a}{\lambda_{\infty}} = r$, a constant, and the equation may be written: $1 - x = r \sqrt[3]{\eta}$.

If now it is assumed that in an aqueous solution of two salts with a common ion the dissociation of each salt is that which it would exhibit if it were present alone at a concentration equal to the sum of the concentrations of the two salts, we have the following formulæ: $1 - x_1 = r_1 \sqrt[3]{\eta_1 + \eta_2}$ and $1 - x_2 = r_2 \sqrt[3]{\eta_1 + \eta_2}$, where x_1 and x_2 are the degrees of dissociation, η_1 and η_2 the concentrations of the two salts in the mixture, and r_1 and r_2 are the constants deduced from the behaviour

of the separate salts. If, further, $\lambda_{1\infty}$ and $\lambda_{2\infty}$ are the maximum limiting values of the equivalent conductivity for the separate salts, and κ_1 and κ_2 are the contributions which the two salts respectively make to the specific conductivity (κ) of the mixture, then we have: $\kappa = \kappa_1 + \kappa_2 = x_1 \cdot \eta_1 \cdot \lambda_{1\infty} + x_2 \cdot \eta_2 \cdot \lambda_{2\infty}$, the values of x_1 and x_2 being calculated by the formulæ given above. Barmwater has shown that in this way it is possible to calculate the conductivity of a mixture of two salts with a common ion in good agreement with the observed value. This result is confirmed by some experiments recorded below, in which the conductivity of mixtures of two iodides in water was determined, although the agreement between calculated and observed values is in this case not quite so close as Barmwater found for mixed chlorides, acetates, and propionates.

When this method is employed, as in the present paper, to calculate the conductivity of a solution of two salts in an organic solvent, it must be borne in mind that there is a little uncertainty as to some of the factors entering into the calculation. First of all, the question arises whether in organic solvents also the equivalent conductivity of a binary salt in dilute solution is a linear function of the cube root of the concentration. Walden, it is true, bases his calculation of λ_∞ for salts in organic solvents on the validity of this relationship (see *Zeitsch. physikal. Chem.*, 1906, 54, 133), but there are other investigators who dispute its accuracy (see Turner, *Amer. Chem. J.*, 1908, 40, 571).

It is further quite fairly pointed out that the extrapolation for λ_∞ in the case of most organic solvents has to be made over a much greater interval than in the case of water, and that the value of λ_∞ obtained by such an extrapolation must be correspondingly less trustworthy. Some recent workers therefore (Turner, *loc. cit.*; Dutoit and Duperthuis, *J. chim. phys.*, 1908, 6, 703), avoid an extrapolation from moderate dilutions, preferring to carry out direct measurements of conductivity at extremely high dilutions. In such measurements, naturally, other sources of error are liable to creep in, and the correction to be applied for the conductivity of the solvent becomes relatively large.

Whatever be the true cause, there are undoubtedly very serious discrepancies in the values of λ_∞ found by different observers for salts in organic solvents. One example of such discrepancy may be quoted. The value of λ_∞ for potassium iodide in ethyl alcohol at 25° found by Walden by extrapolation (*Zeitsch. physikal. Chem.*, 1906, 54, 137) is 53; the value deduced in a similar manner from Jones and Lindsay's figures (*Amer. Chem. J.*, 1902, 28, 339) is 49.2; the value found by the present authors is 51.4. Direct measurements at very high dilutions, on the other hand, lead to lower values for the same

constant; Turner (*loc. cit.*) finds $\lambda_{\infty} = 48.5 \pm 0.5$; Dutoit and Rapport (*J. chim. phys.*, 1908, 6, 545) find $\lambda_{\infty} = 39.2$ (Siemens units) at 18° , a figure which, on conversion into the ordinary units, becomes 46.5 at 25° , the temperature-coefficient being taken as equal to that for tetraethylammonium iodide in ethyl alcohol (Walden, *loc cit.*).

Whilst the occurrence of these discrepancies suggests caution in generalising from recorded experimental data, the results obtained in this first portion of our investigation point fairly definitely to two conclusions. The first of these relates to the change in equivalent conductivity with dilution for the separate salts. As already stated, doubt has been expressed in some quarters whether the equivalent conductivity of a binary salt in an organic solvent is, as in water, a linear function of the cube root of the concentration. The results recorded below are distinctly in favour of the validity of this linear relationship. From about $v = 50$ to $v = 2000$, the equivalent conductivity of tetraethylammonium iodide and potassium iodide in the organic solvents employed is adequately represented by the formula:

$$\lambda = \lambda_{\infty} - a \sqrt[3]{\eta}.$$

The second conclusion which can be drawn from the experimental data recorded below relates to the conductivity of solutions of the mixed iodides. The observed values for the conductivity of these solutions are generally in good agreement with the values calculated by the method which Barmwater has found applicable in the case of aqueous solutions. This indicates that the ionisation of a binary salt in an organic solvent is closely analogous to the corresponding process in water, and that in the one case as in the other, the conductivity of a solution containing two salts with the same negative radicle is such as one would expect on the supposition that the two salts yield a common product of dissociation, and influence each other accordingly. This conclusion is enforced by a comparison of the observed values for the conductivity of solutions of the mixed iodides with the values calculated on the assumption that each iodide makes its contribution to the conductivity of the mixed solution as if the other were not there at all. If one dismisses any preconceived ideas as to the necessity for dissociation, it is conceivable that each salt in the mixed solution makes the same contribution to the conductivity as if it were present alone at the same concentration. The pressure exerted by a mixture of two inert gases is equal to the sum of the pressures exerted by the gases separately, and it is at least conceivable that a similar rule might be valid in connexion with the conductivity of a solution of two salts. The experimental results for the solutions of two iodides in organic solvents are, however, quite opposed to this supposition, for the observed values of the conductivity are in practically every case very much lower than the values calculated on

the assumption that the salts are without influence on each other. In the case of water, which is such a powerful ionising solvent, the differences between the values for the conductivity of the mixed salts calculated on this assumption, and those calculated by Barmwater's method, are not very great, but in the organic solvents the differences are considerable, and the experimental results discriminate clearly in favour of Barmwater's method. The mutual relationship of two salts with a common negative radicle in an organic solvent is therefore intelligible if it is supposed that, as in water, the two salts yield a common product of dissociation.

EXPERIMENTAL.

The salts dealt with in the present communication are tetraethylammonium iodide and potassium iodide. These were employed in the form of the purest commercially obtainable specimens, and a guarantee of the purity of the salts is the agreement between the values of λ_{∞} for their aqueous solutions and the values found by other observers. From the tables below it will be seen that we have found λ_{∞} at 25° to be 111.5 for tetraethylammonium iodide, and 151.2 for potassium iodide. Walden has recorded 112 as the value of λ_{∞} at 25° for tetraethylammonium iodide, and from the latest figures given by Kohlrausch for the ionic conductivities, the corresponding value for potassium iodide should be 151.3.

Solutions of the separate salts were prepared by weighing the dried substance into a measuring flask, dissolving, and making up to the mark at 25° . The more dilute solutions were prepared in the conductivity cell in the usual manner. When a solution containing two salts was to be prepared, a stock solution of each was first made up in the way already described; a measured quantity of each solution was then transferred to a graduated flask by means of a pipette, and the mixture was made up to the mark at 25° with the pure solvent. The conductivity of the solutions was determined in all cases at 25° by the usual Kohlrausch method. Platinised electrodes were employed throughout.

The organic solvents employed in the investigation, namely, methyl and ethyl alcohols, methyl ethyl ketone, acetonitrile, and nitromethane, were carefully dehydrated and fractionated before use. The conductivity of each purified solvent was determined, and subsequently deducted from that of the solutions made up with it. The values found for the specific conductivity of the solvents were as follows: methyl alcohol, 1.0×10^{-6} ; ethyl alcohol, 4.4×10^{-7} — 7.5×10^{-7} ; methyl ethyl ketone, 1.0×10^{-7} ; acetonitrile, 1.6×10^{-6} ; nitromethane, 0.7×10^{-6} — 1.2×10^{-6} . Experiments were made also with

acetone as solvent, but the results obtained were less regular than with the other solvents, and require further investigation.

The experimental results for the solutions are arranged according to the solvents, and under each there are given the conductivity data: first, for the solutions of the separate iodides, and secondly, for the solutions of the mixed iodides. Each table referring to a single salt gives the values of η (in gram-equivalents per c.c.), of λ obs., and of λ calc. The figures for λ calc. have been obtained in the following way (compare Barmwater, *loc. cit.*; McCoy, *J. Amer. Chem. Soc.*, 1908, 30, 1074): first, the observed values of the equivalent conductivity were plotted against the cube root of the concentration, in order to find whether any of the points were obviously off the straight line which was assumed to represent the variation of λ and $\sqrt[3]{\eta}$ in dilute solution. It sometimes appeared that the values for the more concentrated solutions that had been examined lay on a curve, not on a straight line, and these values, therefore, were not used in the subsequent calculations. Apart from these, it was assumed that the relationship between equivalent conductivity and concentration was represented by the formula: $\lambda = \lambda_{\infty} - a \sqrt[3]{\eta}$, and from the ascertained values of λ and η the most probable values of λ_{∞} and a were deduced by the method of least squares. The values so obtained for λ_{∞} and a are recorded at the head of each table, and were used to calculate what λ should be for each value of η ; the figures calculated in this way are tabulated under λ calc. The extent of the agreement between the values of λ obs. and λ calc. is a measure of the validity of the linear relationship between λ and $\sqrt[3]{\eta}$. At the head of each table referring to a single salt there is recorded also the value of $r = \frac{a}{\lambda_{\infty}}$, which is required for the calculation of the conductivity of the solutions containing two salts.

In the tables dealing with the solutions of the mixed salts, η_1 and η_2 are the concentrations of the two salts in the solution, and κ is the observed specific conductivity of the solution. The calculated specific conductivity of each solution is given under the heading $\kappa_1 + \kappa_2$, the values of κ_1 and κ_2 being obtained by the formulæ already discussed.

In order that a comparison may be made between water and the organic solvents, the behaviour of the iodides in aqueous solution has been studied, and the experimental data are incorporated in the tables which immediately follow.

*Water.**Tetraethylammonium Iodide.*

$$\lambda_{\infty} = 111.5; a = 604.5; r = 5.423.$$

$\eta \times 10^6$.	λ obs.	λ calc.
7.986	99.7	99.5
3.993	102.0	101.9
1.996	103.4	103.9
0.998	105.5	105.5
0.499	106.9	106.8
0.249	107.9	107.7

Potassium Iodide.

$$\lambda_{\infty} = 151.2; a = 399.0; r = 2.639.$$

$\eta \times 10^6$.	λ obs.	λ calc.
27.25	139.2	139.2
13.62	141.6	141.7
6.812	143.6	143.6
3.406	145.2	145.2
1.703	146.6	146.4

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6$.	$\eta_2 \times 10^6$.	$\kappa \times 10^6$.	$(\kappa_1 + \kappa_2) \times 10^6$.
0.927	12.016	1792	1794
1.854	6.008	1045	1045
3.708	3.004	805	803
7.416	1.502	961	948

The close agreement between the values of λ obs. and λ calc. in the case of the separate iodides shows that for aqueous solutions of these salts the equivalent conductivity is a linear function of the cube root of the concentration, in harmony with Kohlrausch's rule. In the case of the mixed iodides, the calculated value of the specific conductivity, $\kappa_1 + \kappa_2$, is practically equal to the observed value for the first three solutions, but less for the last solution. The greatest difference, amounting to 1.3 per cent., is found for the mixture containing the largest proportion of tetraethylammonium iodide.

It is interesting to calculate what the conductivity would be on the assumption that the salts are without influence on each other, and that each makes the same contribution to the conductivity of the mixture as if the other were not there at all. These contributions can be calculated by using the formulæ $1 - x_1 = r_1 \sqrt[3]{\eta_1}$ and $1 - x_2 = r_2 \sqrt[3]{\eta_2}$, instead of $1 - x_1 = r_1 \sqrt[3]{\eta_1 + \eta_2}$ and $1 - x_2 = r_2 \sqrt[3]{\eta_1 + \eta_2}$. The figures obtained in this way for the conductivities of the four solutions of tetraethylammonium iodide and potassium iodide are 1806, 1058, 816, and 959 respectively. It is surprising that the last figure is so close to the observed value of the conductivity; possibly the latter may be somewhat in error.

*Methyl Alcohol.**Tetraethylammonium Iodide.*

$$\lambda_{\infty} = 127.2; \alpha = 1570; r = 12.35.$$

$\eta \times 10^6.$	λ obs.	λ calc.
19.63	84.9	84.8
9.81	93.4	93.6
4.90	100.6	100.5
2.45	105.9	106.0
1.23	109.8	110.4
0.61	114.5	113.9

Potassium Iodide.

$$\lambda_{\infty} = 117.1; \alpha = 1182; r = 10.1.$$

$\eta \times 10^6.$	λ obs.	λ calc.
[46.76	77.8]	—
[23.38	84.4]	—
11.69	90.4	90.3
5.84	95.6	95.8
2.92	100.2	100.2
1.46	103.9	103.7

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6.$	$\eta_2 \times 10^6.$	$\kappa \times 10^6.$	$(\kappa_1 + \kappa_2) \times 10^6.$
4.234	18.70	1932	1911
8.468	18.70	2223	2205
8.468	9.35	1525	1536
16.94	3.74	1714	1743

The value of λ_{∞} found for tetraethylammonium iodide is somewhat greater than the value, 124, recorded by Walden, and the value of λ_{∞} for potassium iodide is slightly higher than the figure, 115.6, deduced by extrapolation from Jones and Lindsay's measurements. For both salts, when $v > 50$, there is a linear relationship between the equivalent conductivity and the cube root of the concentration.

From the table referring to solutions of the mixed iodides it will be seen that the calculated value of the specific conductivity is in two cases greater, in two cases less, than the observed value; the biggest difference between the observed and the calculated figures is 1.7 per cent. On the assumption that each salt makes the same contribution to the conductivity as if the other were not present, the conductivities calculated for the four solutions would be 2055, 2410, 1669, and 1842 respectively, figures which are all very considerably higher than the actual values.

*Ethyl Alcohol.**Tetraethylammonium Iodide.*

$$\lambda_{\infty} = 57.1; \alpha = 1187; r = 20.8.$$

$\eta \times 10^6.$	λ obs.	λ calc.
[17.61	28.8]	—
8.805	32.8	32.6
4.402	37.5	37.6
2.201	41.7	41.7
1.10	44.8	44.8

Potassium Iodide.

$$\lambda_{\infty} = 51.4; \alpha = 843.5; r = 16.4.$$

$\eta \times 10^6.$	λ obs.	λ calc.
[14.63	31.6]	—
7.315	35.1	35.0
3.657	38.3	38.4
1.829	41.1	41.1
0.914	43.3	43.2

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6$.	$\eta_2 \times 10^6$.	$\kappa \times 10^6$.	$(\kappa_1 + \kappa_2) \times 10^6$.
1.761	11.704	425	418
3.522	5.852	314	308
7.044	2.926	325	319
14.09	1.463	454	431

According to Walden, λ_∞ for tetraethylammonium iodide in ethyl alcohol at 25° is 60, whilst the corresponding figure for potassium iodide is 53 (see also p. 1264).

The agreement between the observed and calculated values of the specific conductivity for solutions of the mixed salts is not so close as in the case of water and methyl alcohol. The difference is about 2 per cent. for each of the first three solutions, and about 5 per cent. in the last case. The experimental figure is probably in error to some extent in the fourth solution. When the conductivities of the four solutions are calculated on the supposition that the salts are without influence on each other, the figures obtained are 453, 350, 357, and 461. Except in the case of the last solution, the observed values of the conductivity are in much closer agreement with the calculated figures recorded in the table.

*Methyl Ethyl Ketone.**Tetraethylammonium Iodide.*

$\lambda_\infty = 159.3$; $\alpha = 5000$; $r = 31.4$.

$\eta \times 10^6$.	λ obs.	λ calc.
1.585	101.1	101.0
0.792	112.9	113.0
0.396	122.3	122.7
0.198	130.3	130.1
0.099	136.5	136.2

Potassium Iodide.

$\lambda_\infty = 115.5$; $\alpha = 2566$; $r = 22.2$.

$\eta \times 10^6$.	λ obs.	λ calc.
2.081	82.7	82.7
1.040	89.5	89.5
0.520	94.3	94.9
0.260	99.5	99.1
0.130	102.7	102.5

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6$.	$\eta_2 \times 10^6$.	$\kappa \times 10^6$.	$(\kappa_1 + \kappa_2) \times 10^6$.
0.4114	1.194	156	143
0.823	0.597	138	136
0.823	0.2985	110	115
1.646	0.2985	178	184

Tetraethylammonium iodide and potassium iodide are both very sparingly soluble in methyl ethyl ketone, so that the dilutions employed in this solvent were considerably higher than in other cases. The conductivity of methyl ethyl ketone, however, is very low, about 1.0×10^{-7} , and consequently the correction to be applied to the conductivity of these very dilute solutions is smaller than it would

be in the case of other solvents. As regards the mixed salts, the calculated conductivity is less than the observed value for the first two solutions, but greater for the last two solutions. If each salt made its own independent contribution to the conductivity of the mixture, uninfluenced by the presence of the other salt, the figures for the conductivity would be 155, 149, 122, and 194 respectively. Except in the first case, the observed values of the conductivity are much closer to the figures calculated by Barmwater's method, and recorded in the last column of the foregoing table.

Acetonitrile.

Tetraethylammonium Iodide.

$\lambda_{\infty} = 195.1$; $a = 2075$; $r = 10.64$.

$\eta \times 10^6$.	λ obs.	λ calc.
[18.06	142.4]	—
9.03	151.7	151.5
4.515	160.5	160.8
2.258	167.8	167.9
1.129	172.8	173.5
0.564	179.3	177.9

Potassium Iodide.

$\lambda_{\infty} = 200.9$; $a = 2461$; $r = 12.26$.

$\eta \times 10^6$.	λ obs.	λ calc.
[27.49	128.6]	—
13.75	142.3	142.0
6.87	153.9	154.1
3.435	163.3	163.7
1.718	171.6	171.4

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6$.	$\eta_2 \times 10^6$.	$\kappa \times 10^6$.	$(\kappa_1 + \kappa_2) \times 10^6$.
10.752	11.00	2941	2928
10.752	22.00	4149	4069
5.376	22.00	3567	3500
21.504	4.40	3444	3437

A comparison of the values of λ obs. and λ calc. for solutions of the separate iodides in acetonitrile shows that the agreement is not quite so close as in some of the other cases recorded in this paper. The values of λ_{∞} obtained by extrapolation, namely, 195.1 for tetraethylammonium iodide and 200.9 for potassium iodide, are in fair agreement with the corresponding figures recorded by Walden, 200 and 207 respectively.

The values calculated for the conductivity of the mixed iodides, and recorded in the last column of the table, are all somewhat smaller than the observed values, the differences ranging from 0.3—2.0 per cent. The differences are small compared with those between the observed values of the conductivity and the values calculated on the assumption that each salt makes its own contribution to the conductivity of the mixture, uninfluenced by the presence of the other. The values so calculated are 3211, 4504, 3753, and 3660 for the four solutions respectively, figures which are 5—9 per cent. greater than the observed values.

*Nitromethane.**Tetraethylammonium Iodide.*

$$\lambda_{\infty} = 113.8; a = 1069; r = 9.39.$$

$\eta \times 10^6.$	λ obs.	λ calc.
7.84	92.4	92.6
3.92	97.1	96.9
1.96	100.6	100.4
0.98	103.3	103.2
0.49	105.3	105.3
0.245	106.9	107.1

Potassium Iodide.

$$\lambda_{\infty} = 127.8; a = 1734; r = 13.57.$$

$\eta \times 10^6.$	λ obs.	λ calc.
[7.206	92.4]	—
3.603	100.7	101.2
1.801	107.0	106.7
0.9005	111.4	111.0
0.4503	114.6	114.5
0.2251	117.0	117.2

Tetraethylammonium Iodide + Potassium Iodide.

$\eta_1 \times 10^6.$	$\eta_2 \times 10^6.$	$\kappa \times 10^6.$	$(\kappa_1 + \kappa_2) \times 10^6.$
6.448	0.5764	652	656
3.224	1.441	450	449
3.224	2.882	570	581
1.612	2.882	436	441

The value obtained for λ_{∞} for tetraethylammonium iodide is considerably lower than the value, 120, recorded by Walden. The conductivity of potassium iodide in nitromethane has, apparently, not been previously determined.

The observed values for the specific conductivity of solutions of the mixed iodides in nitromethane are, except in one case, *smaller* than the values calculated by Barmwater's method. The differences, therefore, between observed and calculated figures are opposite in sign to those found in most of the other cases. All the greater are the differences between the observed values of the conductivity and those calculated on the assumption that each salt, so far as carrying the current is concerned, acts as if the other were not present; the values calculated for the conductivity in this latter way are 671, 472, 613, and 460 respectively.

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CXIV.—*The Accuracy of the Gold Bullion Assay.*

By JOHN PHELPS.

IN 1893 T. K. Rose (Trans., **63**, 700) showed that by the use of suitable precautions the probable errors of the gold bullion assay could be reduced to ± 0.02 per 1000 in the case of high-grade refined gold.

Previously it had been usually considered that the errors were not less than ± 0.1 per 1000 (13th *Annual Report of the Deputy Master of the Mint*, 1882, p. 47).

Recently a paper* has been communicated to the American Institute of Mining Engineers by F. P. Dewey (Assayer, Mint Bureau, U.S. Treasury, Washington) containing a discussion of the degree of accuracy obtained in gold bullion assays in the United States Mints and Assay Offices, and at the Mint Bureau at Washington. In this paper figures are quoted showing a degree of accuracy far less than that previously attained; a discussion of the degree of accuracy found practicable in the ordinary work of the Assay Office at the Royal Mint during recent years therefore appears desirable. Modifications of the methods employed in 1893 are described by Dr. Rose (35th *Annual Report of the Deputy Master of the Mint*, 1904, p. 70), and the results discussed in this paper have been obtained by the methods there described with some minor improvements.

The muffle furnaces are now heated by gas, each having a row of burners in which the gas and air in each burner can be independently adjusted.

Patent cupels, consisting largely of magnesia, have been found to give a smaller loss of gold, and have been adopted for general use, although with good bone-ash cupels almost equally good comparative results may be obtained.

The loss of gold in cupellation is 0.3 to 0.4 per 1000 with the best patent cupels, and 0.5 to 0.6 with bone-ash cupels; moreover, the greater thermal conductivity of the former facilitates the regulation of the temperature of cupellation.

In this paper the following points are considered, and figures bearing on them are examined from the point of view of the probable errors in the results.

1. Gold assays made in the course of routine work in the assay department of the Royal Mint.

* "The Assay and Valuation of Gold Bullion," *Trans. Amer. Inst. Mining Engineers*.

2. (a) Assays of trial plates and comparisons of samples of fine gold made in the Royal Mint.

(b) Comparison of fine gold made in the Mint laboratory with that produced by the Utrecht Mint.

3. Comparison of the results of assays made in the Royal Mint with the work of other assayers working on the same material.

4. Discussion of the results recorded in the paper by F. P. Dewey (*loc. cit.*).

1.—*Routine Assays at the Royal Mint.*

In the ordinary routine of gold assaying at the Royal Mint, both the "proofs" and the ordinary assays are now weighed to 0.05 per 1000 or 0.025 milligram, some improvements in the balances rendering this convenient. The exact surcharge found from the mean of six proof assays is deducted from all the assays by means of a rider weighing 0.5 milligram.

The mean surcharges and the probable errors calculated by the divergences of individual proofs from their mean are given in table I for twelve of the first 120 batches of gold assays worked in the Mint in 1909; no special selection was made, every tenth fire being quoted, and these represent the quality of the work in the whole 120 fires.

Each batch or "fire" consists of 72 assays, which are arranged in the muffle in twelve rows of six, numbered from left to right, and from front to back. Six proofs are included in each fire in the positions 1, 11, 21, 40, 56, and 72.

TABLE I.

No. of fire.	Fine gold per 1000, in proofs.	Mean surcharge, per 1000.	Probable error, per 1000.	Maximum difference, per 1000.
1	1000	0.77	± 0.018	0.08
11	1000	0.90	± 0.021	0.10
21	916.6	0.87	± 0.017	0.08
31	1000	0.77	± 0.017	0.08
41	916.6	0.84	± 0.022	0.14
51	1000	0.72	± 0.022	0.12
61	916.6	0.70	± 0.009	0.05
71	916.6	0.76	± 0.017	0.09
81	916.6	0.68	± 0.013	0.08
91	916.6	0.38	± 0.022	0.12
101	916.6	0.64	± 0.015	0.09
111	916.6	0.56	± 0.007	0.04

The work of three assayers is here represented.

The average probable errors of the surcharge, which is the mean of six assays, is ± 0.0167 per 1000.

The ordinary assays being weighed with equal care, the probable error of a single assay is ± 0.040 , and after applying the surcharge, ± 0.043 per 1000.

2.—(a) *Trial Plate and Fine Gold Assays made at the Royal Mint.*

This gives examples of the degree of accuracy obtained by the most careful work, weighing to 0.01 per 1000. Table II shows the results obtained in assaying a "working trial plate."

The working trial plate consists of an alloy of gold and silver, and is about 18 troy ounces in weight; when its assay value has been accurately determined it is used for proof assays in the assay of gold coin and coinage bars.

Each determination quoted is the result of six assays compared with six proofs containing very nearly the same amount of fine gold, proofs and assays being made up to contain the same quantities of silver, copper, and lead.

TABLE II.

Determination.	Compared with	Result.	Probable error per 1000.
1	Standard trial plate	916.604	± 0.013
2	" " " "	916.590	± 0.030
3	Fine gold " "	916.649	± 0.010
4	" " " "	916.592	± 0.011
5	" " " "	916.608	± 0.009
6	Standard trial plate	916.613	± 0.009
7	" " " "	916.627	± 0.016
8	Fine gold " "	916.587	± 0.008
	Mean.....	916.609	± 0.0057

The mean probable error deduced from the "results" alone is ± 0.0072 , which is somewhat greater than the mean of the probable errors of the results, as it is increased by errors due to differences of sample and any inaccuracy in the value (916.60) assigned to the standard trial plate.

In determinations of this kind three concordant results are usually considered sufficient, the large number of assays made in this case being due to the comparatively large difference of series 3 from the previous two.

It is satisfactory to find that even in a set of assays including rather widely divergent results so low a value for the probable error can be obtained. Even a considerably larger number of assays would scarcely justify a much greater confidence in the result, although the probable error would be reduced. Dr. Rose's conclusion in 1893, however, may perhaps be modified to the extent of claiming an accuracy of ± 0.01 per 1000 for the mean of a considerable number, say 20 or more, assays.

The weighing error on a single observation being 0.01 per 1000 in this work, it does not seem likely that more accurate weighing, if such were practicable, would materially improve the results.

2.—(b) *Comparison of Fine Gold made in the Mint Laboratory with that produced by the Utrecht Mint.*

In 1907 samples of the fine gold used for "proof" or check assays were exchanged between the Royal Mint and the Utrecht Mint.

The results obtained by a comparison of these samples of fine gold are given in table III, each determination consisting of the comparison of six assays of each sample.

The assays were made with all known precautions and weighed on a balance indicating 0.01 per 1000 or 0.005 milligram.

TABLE III.

No. of determination.	Fineness of Utrecht gold.	Probable error per 1000.
1	999.960	—
2	999.980	± 0.015
3	999.978	± 0.020
4	999.982	± 0.025
Mean of 2, 3, and 4	999.980	± 0.012

The Mint proof gold is taken at 1000.00 in each case.

The assays in the first determination are not included in the mean, as the Utrecht gold was in that instance assayed exactly as received, whilst in the other cases it was previously scraped on the surface with a steel knife; this treatment has been found to effect an improvement in the fineness of gold, particularly if it has been kept some time after rolling out.

3.—*Comparison of the Results of Assays made in the Royal Mint with the work of other Assayers on the same material.*

Ingots of refined gold are received at the Mint from the Bank of England, for coinage, with the report of an assayer acting on behalf of the Bank, who reports each ingot to 0.1 per 1000 on the result of three assays made of a single sample cut from one end of the ingot.

A sample is cut from the other end and assayed at the Mint. When the assays agree within 0.1 per 1000 with the Bank assayers the result is taken as the assay of the ingot; if a difference of 0.2 or 0.3 per 1000 is found the ingot is reported at an intermediate value.

In all cases where the Bank assay differs by more than 0.3 per 1000 from the first Mint assay the latter is repeated. If the difference between the assays is such as to indicate a difference in composition of different parts of the ingot, assay samples are taken from both ends, and the ingot is reported at the mean value if the extreme variation does not exceed 1.0 per 1000.

Large differences in composition are very rare, and are never found in gold of 995 fine and upwards.

Table IV shows the proportion of assays which differed by more than 0.2 per 1000 from the final result in two consignments of gold ingots submitted for coinage during the past year.

TABLE IV.

Assayer.	No. of ingots.	Assays differing from final result by 0.3 per 1000 or more.	
		Number.	Percentage.
<i>A</i>	1018	96	9.43
<i>B</i>	913	23	2.52
<i>C</i>	953	26	2.73
<i>D</i>	1014	17	1.68
All Bank assayers	3898	162	4.16
Original Mint assays...	3898	93	2.39

In 1908, 378 ingots were received at the Mint with reports of the United States Mint, which had refined the gold. Each melting, producing about ten ingots, is understood to be valued by the U.S. Mint on the assay of two samples, and is reported to 0.25 per 1000.

Of these 378 ingots 19 were found on repeated assay to be 0.3 or more per 1000 different from the U.S. Mint report, the percentage of incorrect assays being 5.0. Of the original Mint assays, only 4, or 1.06 per cent., were found incorrect by 0.3 or more per 1000 on re-assay.

4.—Results published by F. P. Dewey.

F. P. Dewey (*loc. cit.*) tabulates the results of assays of gold 999.8 fine, of which he says: "On the whole, the figures may be taken as fairly representing the ordinary run of commercial work upon such high-grade bullion."

Of the 87 assays quoted, 33.5 per cent. differ by 0.3 per 1000 or more from the mean value reported, the average difference of the individual assays from their mean being 0.19 per 1000.

The probable errors in the four sets of assays quoted are given in table V.

TABLE V.

Sample of gold.	No. of assays.	Probable error per 1000.
1	20	± 0.041
2	20	± 0.040
3	19	± 0.036
4	28	± 0.029

These values of the probable error are very high considering the large number of assays made, and correspond with an error of not less than ± 0.15 per 1000 on a single assay.

In table VI an attempt has been made to compare the probable

errors of a single gold bullion assay made in different laboratories, as deduced from the figures quoted.

The figures assigned to the Bank assayers' results and to those of the United States Mint are deduced from the comparison of the results with subsequent assays of the same material at the Royal Mint; the others are calculated by means of the usual formulæ from the differences of individual results from their mean.

TABLE VI.

Authority or assayer.	Probable error per 1000.
Royal Mint: ordinary assays—single assay	± 0.043
" " trial plate comparisons—single assay ...	± 0.023
Trade assayers (London)—single assay	± 0.081
" " " triple "	± 0.057
United States Mint (10 ingots by 2 assays).....	± 0.062
" " Mints (F. P. Dewey)—single assay.....	± 0.150

In conclusion, the author has to thank Mr. S. W. Smith for permission to include in the results tabulated above the figures of assays made by him, and Dr. T. K. Rose for permission to quote assays made at this Mint.

ROYAL MINT.

CXV.—*Acetone Derivatives of d-Fructose.*

By JAMES COLQUHOUN IRVINE and CHARLES SCOTT GARRETT, B.Sc.
(Berry Scholar in Science).

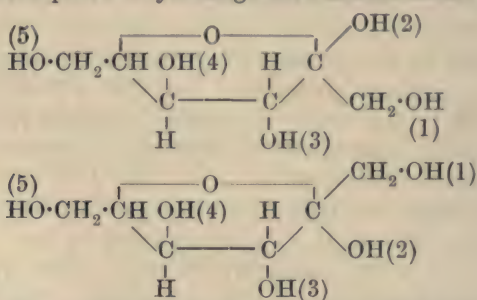
THE condensation of sugars with aldehydes or ketones gives well-defined compounds, the constitution of which has given rise to some discussion. With respect to their non-reducing properties, ready hydrolysis, and in the absence of mutarotation, these substances resemble the artificial glucosides; they differ from the latter in their resistance to the action of enzymes, and also in the fact that in their formation at least two hydroxyl groups of the sugar molecule must be substituted.

In certain cases, the formation of sugar derivatives containing one such residue in combination is succeeded by condensation with a second molecule of the aldehyde or ketone. Thus, glucose gives a definite glucosemonoacetone as the first step in the formation of the diacetone compound, but the reaction is complicated by the necessity to convert the sugar into glucose dimethylacetal in the first stage of the process. From the constitutional point of view this is an objection, and we have accordingly confined our attention in the present paper to the simpler case of the condensation of *d*-fructose with acetone. Fischer has shown (*Ber.*, 1895, **28**, 1164) that the main product of this reaction is a diacetone compound,

which he termed the α -form. A minute quantity of a stereoisomeride (m. p. 97°) was also isolated, and, without further examination, was termed β -fructosediacetone. This substance was obtained by Fischer on one occasion only, and the conditions governing its formation could not be ascertained. These isomerides are doubtless to be regarded as derivatives of α - and β -fructose respectively, and in a recent paper (Trans., 1909, **95**, 1220) it was shown that in the formation of the α -compound the acetone reacts as a ketone, and is not attached to one of the primary alcohol groups. The suggestion was also made that the acetone residues were combined in the form of five-membered rings, but it must be admitted that the exact linking of ketonic residues to polyhydric alcohols or sugars is still uncertain. According to Fischer (*loc. cit.*, p. 1169), the condensation probably involves hydroxyl groups attached to β -carbon atoms, and the results obtained by Purdie and Young (Trans., 1906, **89**, 1196) in the case of acetonerhamnoside point to the same conclusion.

We are at present making a study of the condensation of ketones with polyhydric compounds, and, pending the publication of our results, it is premature in the present paper to allocate the ketonic residues in the fructoseacetones in either five- or six-membered rings, but the results which we now submit are most readily explained on the assumption that the ketonic groups are present in the α -linking.

Consideration of the stereochemical formulæ for α - and β -fructose shows that, in addition to diacetone derivatives, each form of the sugar should be capable of yielding three monoacetone compounds:



To facilitate description of the compounds, the hydroxyl groups are numbered, and the possible positions in which the acetone residues may be linked so as to form five-membered rings are tabulated below:

	Hydroxyl groups substituted.	Nature of product.	No. of isomerides.
A	1 : 2	Glucosidic	2 (α and β)
B	2 : 3	"	2 "
C	3 : 4	Reducing	2 "

It should be possible to distinguish between these different isomerides, as only compounds of the type A and C would be capable of condensing with a second molecule of acetone to give fructosediacetones. On the other hand, the compounds B would, in all probability, fail to undergo further condensation.

We have succeeded in isolating the α -form of the type A, and a syrup which corresponds in its reactions with B. Evidence has also been obtained of the existence of β -fructosemonoacetone of the type A, but no compounds corresponding with C have been isolated, and we conclude that the first reaction between the ketone and the sugar invariably involves the reducing group of the latter. The condensation apparently follows the simplest possible course, the first acetone residue becoming attached in positions 1 and 2, the second in 3 and 4, while simultaneously a quantity of the 2:3-monoacetone is formed which is incapable of further condensation.

It is difficult to establish this mechanism of the reaction by direct experimental methods. Pure dry fructose is practically insoluble in cold acetone, and, although the solubility is much increased by the presence of small quantities of hydrogen chloride, the condensation then proceeds rapidly, and polarimetric examination showed a continuous increase to a constant value in the *l*avorotatory power. No evidence of the intermediate formation of monoacetone compounds was thus obtained, and the products isolated before the reaction was complete consisted of free fructose together with α -fructosediacetone. No unaltered sugar was, however, present when the solution of fructose in acid acetone attained a constant rotatory power. The products then consisted of α - and β -fructose-diacetones and an uncrystallisable glucosidic syrup, amounting to over 40 per cent. of the fructose used. This syrup had the composition of a fructosemonoacetone, and evidently contained β -fructosemonoacetone, as, on further treatment with acid acetone, it was partly converted into the β -diacetone compound. As we find that under the conditions of this experiment no interconversion of the isomeric fructosediacetones takes place, the formation of the β -form points conclusively to the presence of β -fructosemonoacetone in the original syrup. The bulk of the syrup, however, was recovered unchanged, and its identity as a monoacetone compound was confirmed by conversion into a volatile trimethyl derivative by means of the silver oxide reaction. It thus corresponds in properties with the type B, and doubtless consists of a mixture of α - and β -forms.

Fructosemonoacetone was obtained by the partial hydrolysis of α -fructosediacetone by means of very dilute aqueous hydrogen chloride. The isomeric fructosediacetones show a marked difference

in their behaviour towards hydrolytic agents, the α -compound being much more readily hydrolysed than the β -form. The latter resists the action of 0.1 per cent. of hydrogen chloride up to 60°. At higher temperatures the compound is completely hydrolysed, and, judging from the initial decrease and subsequent increase of lævoptatory power, the two ketonic residues are removed simultaneously but at different rates. On the other hand, the α -isomeride shows the successive removal of the acetone groups in marked fashion, the hydrolysis with the same concentration of acid proceeding readily at 20°, and under these conditions only the non-glucosidic group is removed. No indication of this hydrolysis in definite steps is obtained at higher temperatures than 30°.

The progress of the reaction was in each case followed polarimetrically, and in the accompanying diagram the changes are plotted in curves, the abscissæ representing time in hours, and the ordinates the specific rotations calculated on the concentration of the diacetone compound initially present.

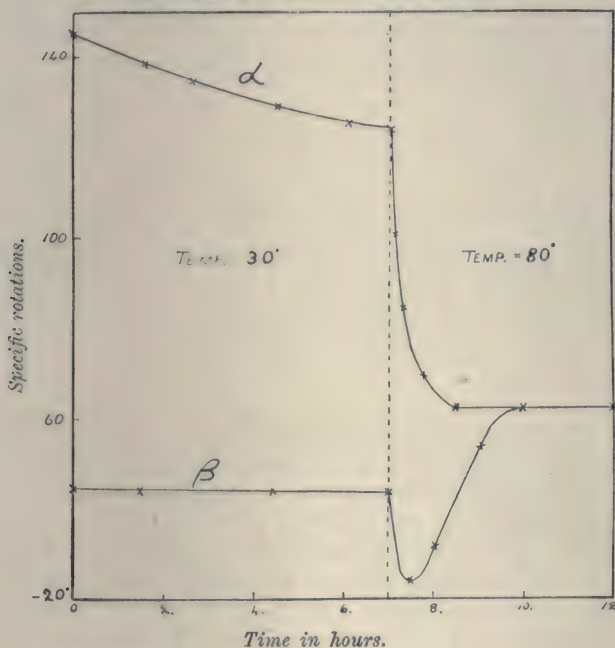
The curve for the α -compound shows a fall to a constant value at 30°, corresponding with the formation of glucosidic α -fructose-monoacetone, and a subsequent fall at 80° to a second constant value, which, when corrected for the concentration of the sugar formed, gives $[\alpha]_D^{20^\circ} - 90.3^\circ$ (fructose = -92°). On the other hand, the curve for the β -isomeride shows the simultaneous removal of the acetone groups at different speeds, and the ultimate formation of fructose. As the curves are similarly directed during the removal of the more unstable acetone residue, it follows that the intermediate monoacetone compounds formed must be stereoisomeric and not identical. The non-glucosidic acetone group is thus the first to be removed in each case. α -Fructosemonoacetone melted at 120—121°, gave $[\alpha]_D^{20^\circ} - 158.9^\circ$ in aqueous solution, and behaved like a glucoside towards Fehling's solution. When condensed with acetone it gave α -fructosediacetone.

We have adhered to Fischer's nomenclature in describing these compounds, but it should be pointed out that the analogy to α - and β -glucosides is not maintained in some respects. Thus the α -form, as stated, is more easily hydrolysed than the β -isomeride. As will be seen from the curves, this holds true, not only for the removal of the acetone residue from the 3:4-position, but also for the glucosidic acetone group. Selective hydrolysis by enzymes cannot, in this case, be applied as a test of configuration, as our results showed that both the α - and β -compounds resisted the action of emulsin, maltase, invertase, or yeast extract. Considering the great instability of the ketonic residues, this result is significant, and, in view of the similar experience of other workers, it would

appear that hydrolysis by enzymes is only effective when the group condensed with the sugar does not form a new internal ring in the aldose or ketose molecule.

A curious relationship is shown by the optical rotatory powers of α -fructosemonoacetone and α -fructosediacetone. In similar concentration, the specific rotations of the two compounds in aqueous solution are practically identical, the values found being respectively $[\alpha]_D^{20} -158.9^\circ$ and $[\alpha]_D^{20} -161.3^\circ$. A similar relationship

Hydrolysis of α - and β -fructosediacetones.



in rotatory power is shown by the corresponding derivatives of glucose:

	$[\alpha]_D$	Difference for glucosidic acetone group.	Difference for two acetone groups.
α -Glucose	+110°	} -121°	} -128°
α -Glucosemonoacetone ...	-11		
α -Glucosediacetone	-18		
α -Fructose	-104°	} -55°	} -57°
α -Fructosemonoacetone ..	-159		
α -Fructosediacetone	-161		

As usual, the optical effect of substitution in the glucosidic position is considerable, but the introduction of the second acetone group in the above cases has very little influence on the rotation.

We are extending our observations with the view of ascertaining if this optical relationship can be correlated with configuration.

EXPERIMENTAL.

Condensation of d-Fructose with Acetone.

The fructose was finely powdered, sifted through fine muslin, and dried in a vacuum before use. A weighed quantity was mixed with sufficient acetone containing 0.2 per cent. of hydrogen chloride to make a 1 per cent. solution of the sugar. The mixture was shaken vigorously until a clear solution was obtained. As a rule, polarimetric readings of the filtered liquid could be taken about twenty minutes after the first contact of the solvent:

Time in minutes.	12.	30.	50.	200.	400.
$[\alpha]_D^{20^\circ}$ $c=1$	—	-135°	143	158	158
$[\alpha]_D^{20^\circ}$ $c=0.5$	-110°	128	135	150	154

The result indicates extremely rapid condensation, and shows that the β -compounds can only be produced in small quantity. By stopping the reaction when the polarimetric values showed that the condensation was incomplete, and treating the solution in the manner described by Fischer, it was possible to isolate the products at different stages. The results thus obtained are included in the introduction.

β -Fructosemonoacetone and 2:3-Fructosemonoacetones.

In separate experiments, 150 grams of fructose (from inulin) were condensed with acetone according to Fischer's directions, and the α -fructosediacetone was removed as usual. The syrup, which in the course of the preparation was precipitated from ethereal solution by the addition of light petroleum, was purified by reprecipitation and extraction with boiling ether. The product, which amounted to 42 per cent. of the weight of fructose used, was a clear, neutral, deliquescent syrup, sparingly soluble in ether, readily dissolved by alcohol or acetone. It reacted like a glucoside with Fehling's solution. On analysis of a specimen dried at $100^\circ/15$ mm., figures were obtained which agreed approximately with the values calculated for fructosemonoacetone. On now repeating the treatment with acid acetone for twenty hours and boiling the syrupy product with light petroleum, a quantity of β -fructosediacetone was extracted. The compound separated on cooling the solvent, and was identified by analysis and by a determination of specific rotation.

The condensation of the syrup with acetone was again repeated, but the bulk of the material was recovered unaltered, and only a trace of the β -diacetone was extracted. As the syrup now reduced Fehling's solution slightly, it apparently contained some free

fructose, and possibly also a little methylfructoside. To remove these impurities, an aqueous solution was fermented with yeast, filtered, evaporated to a syrup in vacuum, and extracted with cold absolute alcohol. The solution was then decolorised, the solvent removed, and the residue dried at $100^{\circ}/15$ mm. After this treatment, the reaction with Fehling's solution was negative:

Found, C=47.62; H=6.90.

$C_9H_{16}O_6$ requires C=49.09; H=7.27 per cent.

We regard the syrup as a mixture of the α - and β -forms of 2:3-fructosemonoacetone, which is incapable of condensing with a second molecule of the ketone. The substance gave $[\alpha]_D^{30} -17.4^{\circ}$ in aqueous solution, showed no mutarotation, and was not affected by boiling with water for thirty minutes. When heated with 1 per cent. of aqueous hydrogen chloride at 100° , it was completely hydrolysed to give fructose.

Trimethylfructosemonoacetone. — As the compound described above could not be obtained in a crystalline state, and gave an amorphous acetyl derivative unsuitable for analysis, it was definitely characterised by conversion into trimethylfructosemonoacetone. The methylation was conducted as in the case of methyl glucoside, and, on fractionation of the product, a colourless, mobile liquid was obtained (b. p. $120^{\circ}/15$ mm.):

Found, C=54.70; H=8.47; OMe=33.7.

$C_9H_{18}O_3(OMe)$ requires C=54.96; H=8.39; OMe=35.5 per cent.

The compound displays the usual solubilities and reactions of alkylated sugar derivatives of a glucosidic nature, and its formation shows that the syrup under examination was essentially a fructosemonoacetone containing three hydroxyl groups.

Comparative Hydrolysis of α - and β -Fructosediacetones.

One per cent. solutions of each isomeride were prepared in water containing 0.1 per cent. of hydrogen chloride, and the solutions examined polarimetrically in jacketed tubes. Readings were taken at 20° until the rotation was permanent, after which the temperature was raised, by increments of 10° , to 50° . Some of the results are appended:

Time from start.	Temperature.	α -Form.	β -Form.
5 minutes	20°	$[\alpha]_D^{20} \left\{ \begin{array}{l} -145.3^{\circ} \\ 129.4 \end{array} \right.$	-35.7°
275 „			35.7
280 „	30	$[\alpha]_D^{30} \left\{ \begin{array}{l} 128.3 \\ 125.0 \end{array} \right.$	40.5
400 „			40.5
1000 „	50	$[\alpha]_D^{50} \left\{ \begin{array}{l} 58.8 \\ 51.5 \end{array} \right.$	$[\alpha]_D^{20} \left\{ \begin{array}{l} 35.7 \\ 35.7 \end{array} \right.$
1500 „			

The hydrolysis of the β -form only became apparent at 60° .

Hydrolysis at 80°.—The strength of acid used was the same as before, the solution in this case being heated in a thermostat:

Time, in minutes, from start.		15.	30.	90.	180.	380.
$[\alpha]_D^{20}$	β -form	-26.1°	24.4	44.2	62.2	62.7
$[\alpha]_D^{20}$	α -form	-104.4°	75.1	63.2	62.5	62.5

The above experiments gave the conditions under which α -fructosemonoacetone may be prepared.

α -Fructosemonoacetone.—The following are the details of one typical preparation. Ten grams of α -fructosediacetone were dissolved in 500 c.c. of water containing 0.1 per cent. of hydrogen chloride. The solution was kept in a thermostat at 30°, and polarimetric readings taken at intervals. After four and a-half hours the specific rotation, calculated on the initial concentration, was -128°, and as this agrees with the first minimum on the curve, the reaction was accordingly stopped. The acid was removed by shaking with silver carbonate, and the solvent evaporated at 30°/15 mm. The residue was dissolved in ether, filtered from traces of silver, and the solution evaporated to dryness. The product then crystallised in large, star-shaped aggregates of prisms, and was purified by crystallisation, first from a mixture of high boiling petroleum and methyl alcohol, and afterwards from hot ethyl acetate. Yield=8.5 grams; m. p. 120—121°.

Solvent: Water, $c=1.079$; $l=2$, $\alpha^{20} - 3.43^\circ$; $[\alpha]_D^{20} - 158.9^\circ$.

The value remained unaltered after several days. Analysis gave:

Found, C=49.17; H=7.20.

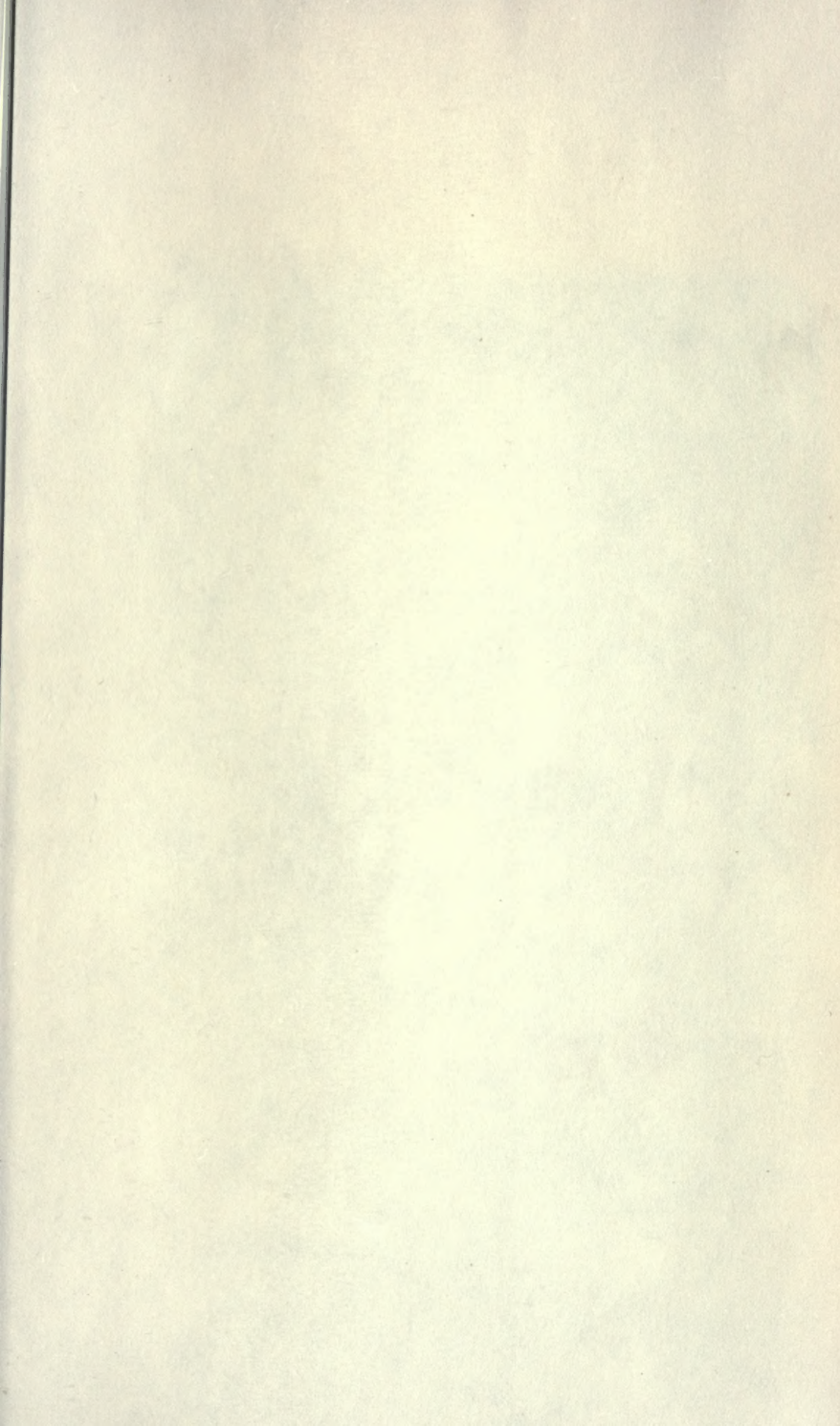
$C_9H_{16}O_6$ requires C=49.09; H=7.27 per cent.

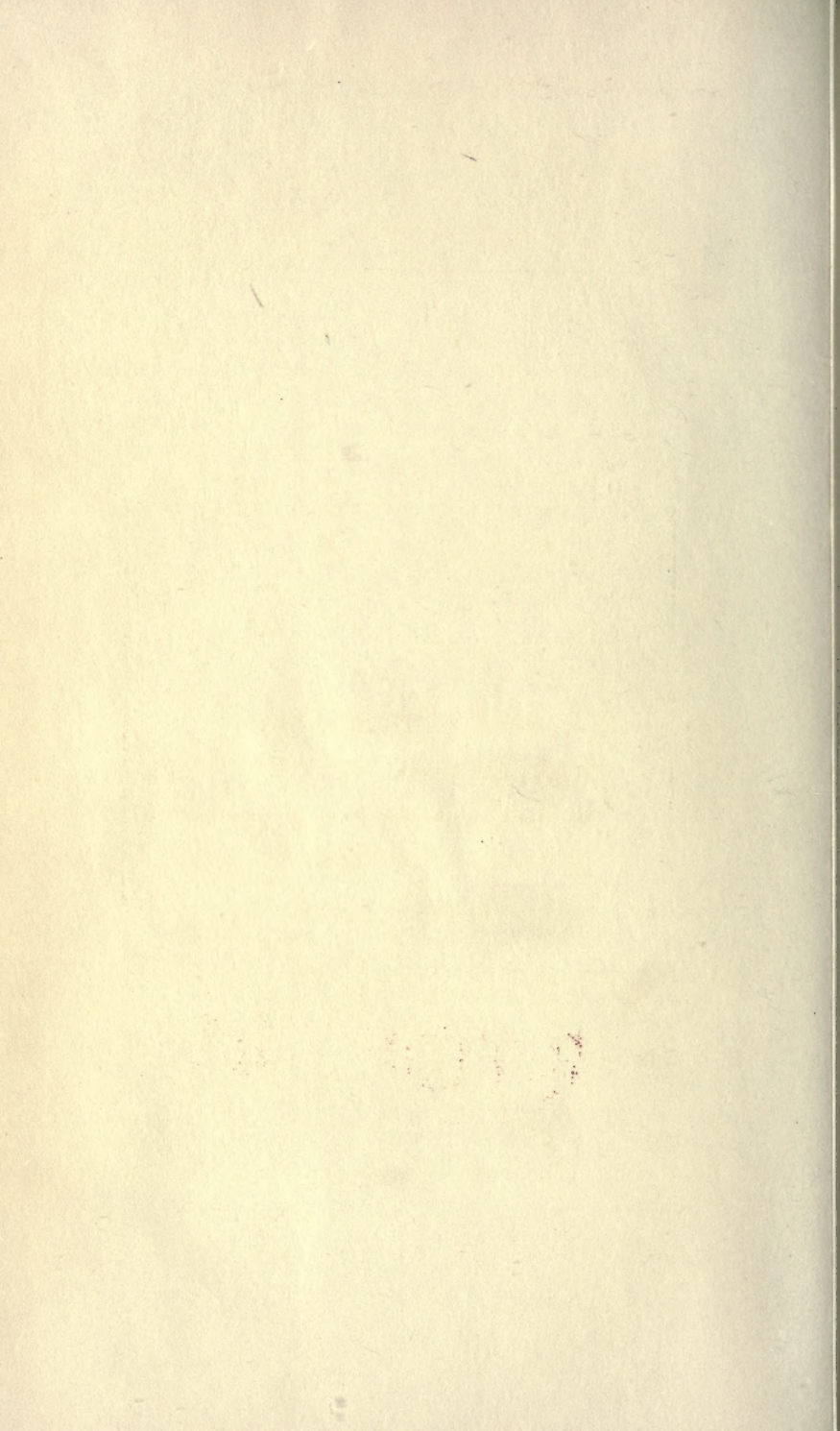
The solubilities of the compound are intermediate between those of fructose and α -fructosediacetone. As the melting point and specific rotation are almost identical with those of the diacetone compound from which it was prepared, further examination was considered necessary. In duplicate experiments, the two compounds were treated at 30° with 0.1 per cent. aqueous hydrogen chloride, polarimetric readings being taken at intervals. The rotatory power of the monoacetone compound remained constant ($[\alpha]_D - 158.4^\circ$) for 250 minutes, and during this time the specific rotation of the diacetone derivative decreased from -155.6° to -130.8°.

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